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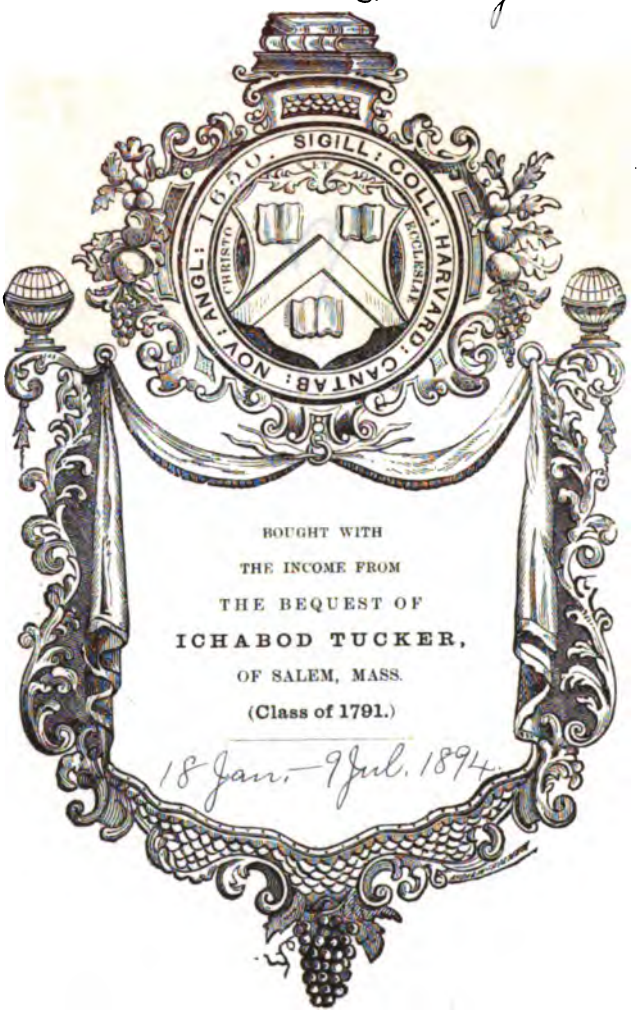

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IN ALL ITS APPLICATIONS TO

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WILLIAM CROOKES, F.R.S., &c.

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JOURNAL OF PHYSICAL SCIENCE

Edited by Wm. Crookes, F.R.S.] (WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE") [Established Forty-Eight Years.

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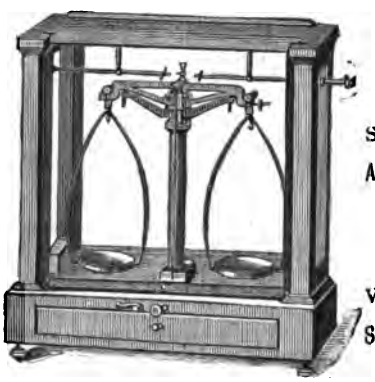

FIG. 3a.

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EDITED BY WILLIAM CROOKES, F.R.S., &c.

No. 1780.—JANUARY 5, 1894.

THE POLARISCOPE IN RELATION TO CHEMICAL CONSTITUTION.*

By PERCY FRANKLAND, Ph.D., B.Sc. (Lond.), F.R.S., Professor of Chemistry in University College, Dundee, St. Andrews University.

ALTHOUGH I come here this evening with great pleasure, I come also with much diffidence and asking your indulgence, for I observe from the numbers of your *Transactions* which have come into my hands that you are accustomed to be addressed on these occasions by those who are more or less actively engaged in the practice of brewing, and who select, therefore, also such practical subjects for their discourses as will be of actual service in the course of your industrial work.

In responding to the invitation of your Secretary to address you to-night, I have ventured to depart from the usual practice of my predecessors in bringing before you a subject which is of no direct practical or pecuniary moment to brewers, but which, nevertheless, it appears to me, may be of considerable interest to all such as follow with intelligence what I am of opinion should be one of the most intellectual and scientific of all the industries.

In every modern brewery continual use is made of an instrument which is capable of revealing one of the most remarkable properties possessed by only a comparatively small number of substances, viz., the power of rotating the plane of polarisation of a beam of polarised light which is transmitted through them. The instrument in question is known as the polariscope or polarimeter, and inasmuch as some of the most important substances which display the power of rotating the polarised beam are the sugars, it is not unfrequently also called the saccharimeter or sugar measurer.

The construction and principles underlying the use of this instrument must be so well known to all of you, that it is quite unnecessary for me to enter into any description of them, nor into its use in the brewery. On the other hand, I will endeavour to give you some account of what has been accurately ascertained concerning those substances which possess the remarkable property of affecting this instrument, and which, on account of their rotating the plane of polarisation, we generally speak of as *optically active bodies*.

The existence of such active substances possessing the power of rotating the plane of polarisation was discovered by Arago in 1811 on rock crystal, whilst four years later —in 1815—Biot found that certain organic substances were possessed of the same property, and during no less than forty years he laboured in investigating these phenomena of circular and rotatory polarisation and in ascertaining the laws by which they are governed.

It is, however, with the connection between this property of optical activity and the chemical character of the substances possessing it that we are specially concerned this evening.

The great pioneer in the special study of these active substances from a chemical point of view was Pasteur, and there is nothing more indicative of the marvellous fertility of his genius than the manner in which, whatever he has touched, has proved to be a solid foundation-stone on which it has become possible to subsequently erect an edifice of vast and imposing proportions. Thus, in this case, his remarkable prescience led him to see that the study of these optically active substances must ultimately result in the most important revelations concerning the internal arrangement of matter, and by the brilliancy of his initial discoveries in this direction he drew the attention of a number of other chemists to this subject, the investigation of which has been rewarded by some of the most signal and profound advances in chemical science during recent years.

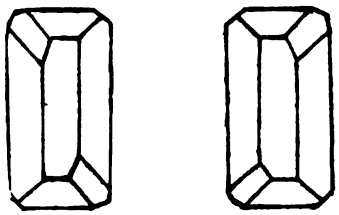
Already, in 1861, more than thirty years ago, Pasteur pointed out that this optical activity was associated in a most remarkable manner with crystalline form, for he observed that those substances which possess this activity exhibit a lack of symmetry in their crystalline structure.

Moreover, in those cases in which a substance was known to exist in two different varieties, *the one turning the plane of polarisation to the left, and the other, through the same angle, to the right*, he observed that there existed the most extraordinary relationship between the crystals of these two varieties, or optical isomers as we call them.

This relationship of form is well exemplified by the

* A Paper read before the North of England Institute of Technical Brewing, Manchester, Oct. 20th, 1893.

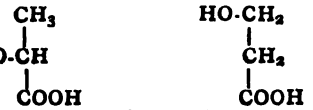
following diagram of the crystals of dextro- and lævo-ammonium bimalate :—



On looking carefully at these two forms it will be observed that they are not superposable the one on the other, but, like our two hands, the one is the image of the other as seen in a mirror. To this relationship subsisting between an object and its non-superposable mirror image, those who delight in long words give the name of "*enantiomorphism.*"

Pasteur did not remain satisfied with this superficial observation, but was carried by his imagination to speculate on the internal structure of these bodies exhibiting this remarkable external relationship, and, with that courage which has characterised his career, he at once proclaimed his belief that the constituent atoms of these substances were arranged also in some way or other in a dissymmetric manner, and that the dissymmetry of the lævo-rotary body must be the non-superposable dissymmetry of the dextro-rotary substance as seen in a mirror.

The great source of difficulty which these optically active substances caused chemists was the circumstance that the difference between them could not be represented by the customary formulæ. Thus, to take the simplest case of lactic acid, $C_3H_6O_3$; of this substance we can predict by formulæ the following varieties, or *isomers* as we call them :—



But not only are these two lactic acids known and easily distinguishable, but the first form we know in no less than three modifications, which hardly differ from each other excepting in their action on polarised light; thus one of them has no action on polarised light at all, or is *optically inactive*, whilst, of the other two, the one turns the plane of polarisation to the right and is called *dextro-rotary*, and the other turns the plane of polarisation through the same angle to the left, and is therefore called *lævo-rotary*. It was Wislicenus who first pointed out that these optical differences could not be represented by differences of ordinary formulæ, and that the ordinary formulæ were inadequate for the purpose in consequence of their not representing the disposition of the atoms in space.

A deliberate and bold attempt was now made to represent the arrangement of the atoms in the three dimensions of space by Le Bel in France, and simultaneously but independently by Van 't Hoff in Holland, and the brilliant results which have rapidly followed on the introduction of their hypothesis have rendered their names amongst the most famous in the annals of chemistry.

These chemists assumed that the atom of carbon may be represented by a tetrahedron, the four groups with which it can combine being attached to the four corners of the tetrahedron.

With the assistance of this hypothesis the explanation of the observed phenomenon of isomerism in lactic acid becomes perfectly easy. Thus these two solid formulæ (Fig. A) represent the lævo- and dextro-rotary lactic acids, whilst the inactive lactic acid consists of equal parts of these two; so that the activity of the one is exactly neutralised by the equal but opposite activity of the other.

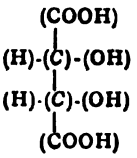
It will be seen that these two solid formulæ are in precise harmony with the previous speculation of Pasteur, that the dissymmetric arrangement in the two opposite optical isomers is not superposable, but bears the relationship of an object to its image as seen in a glass.

To such a carbon atom which is capable of having its four attached groups arranged round it in two different ways, Le Bel and van 't Hoff gave the name or "*Asymmetric*," the one necessary condition for such asymmetry being that all the four attached groups must be different. If two of the groups are identical then the asymmetry ceases, thus :—(see Fig. B) are superposable, and therefore identical.

It is needless to say that a theory so bold and speculative met with the most strenuous opposition, and even ridicule, in many quarters, but so satisfactorily did it explain almost all the cases of optical isomerism which were known at the time that Le Bel and van 't Hoff did not hesitate to proclaim its perfectly general validity and application.

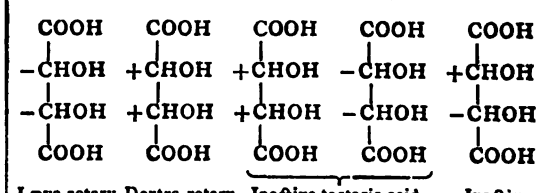
Thus these chemists predicted that all substances which contain such an asymmetric carbon atom must be capable of existing in two forms differing only in their equal but opposite action on polarised light, whilst conversely that all substances exhibiting optical activity must contain at least one asymmetric carbon atom. It is surely one of the greatest triumphs of chemical philosophy that although this bold generalisation has been before the scientific world since 1874, there has not been found a single fact which is in antagonism to it, whilst, on the other hand, innumerable fresh observations have been made corroborating it, and it has been instrumental in stimulating the most important researches.

Let us apply this theory of the asymmetric carbon atom to a substance of somewhat greater complexity than lactic acid, viz., tartaric acid. To this body chemists have on the most overwhelming evidence assigned the formula—



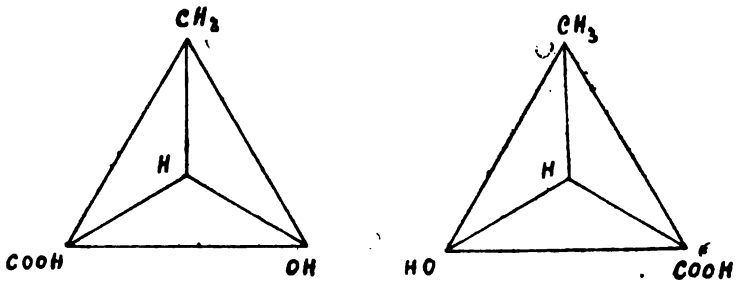
from which it is apparent that it contains two asymmetric carbon atoms, marked (*C*) in the formula.

The four groups attached to each of these carbon atoms must, therefore, be capable of two different arrangements, and it is obvious that if these arrangements fortify each other we shall have a lævo-rotary tartaric acid on the one hand, and a dextro-rotary tartaric acid on the other, and by mixing equal parts of these optically active acids we shall obviously obtain an inactive tartaric acid. But let us suppose that the arrangement of the four groups around the one carbon atom is opposite to the arrangement of the four groups around the other carbon atom, then the lævo-rotation induced by the presence of the one asymmetric carbon atom will be destroyed by the dextro rotation of the other asymmetric carbon atom, and we shall again obtain an inactive tartaric acid different, however, from the one we have considered before. Now as a matter of fact four different tartaric acids—and only four—are actually known, which we may represent thus :—



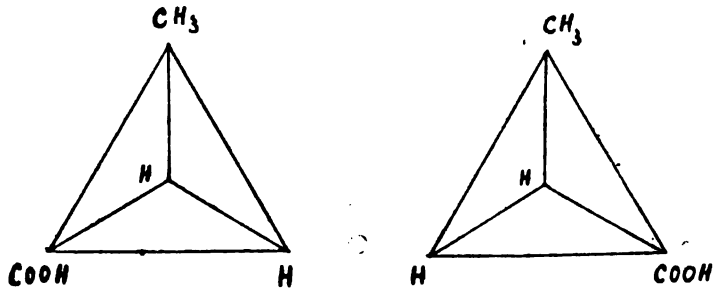
Lævo-rotary tartaric acid. Dextro-rotary tartaric acid. Inactive tartaric acid, commonly known as racemic acid. Inactive tartaric acid proper.

FIG. A.



Dextro- and Lævo-Lactic Acids.

FIG. B.



Practically the fundamental difference between racemic and really inactive tartaric acid, is that from racemic acid we can obtain by suitable means both the active acids, whilst inactive tartaric acid proper cannot in any way be decomposed so as to yield the active tartaric acids, or in other words the inactivity of racemic acid is due to *external compensation*, the inactivity of inactive tartaric acid proper to *internal compensation*. A more complete and conspicuous coincidence between theory and practice than is furnished by the case of these four tartaric acids it is difficult to imagine, and necessarily leads us to place a confidence in the theory which further experience has abundantly proved to be well bestowed.

(To be continued.)

WORK OF THE COMMITTEES ON THE "INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL."*

By JOHN W. LANGLEY, Cleveland, Ohio.

THE history of the organisation and work of these committees up to the present year is briefly as follows:—

In the summer of 1888 it was the fortune of the present writer to present the subject of the desirability of establishing a set of samples of steel which should be analysed with extreme care, in order that they might become standards to which scientific and commercial analyses of iron and steel could be subsequently referred; also, that greater uniformity in the results of analyses might be brought about, since these standards would bear towards analytical methods somewhat the position which the original units of weight and length, the grm. and metre, or the pound and yard, do to the mechanical arts.

The plan met with hearty co-operation, with the result that committees were appointed in Sweden, Germany, France, England, and America to receive the material and see that the necessary analyses were executed.

These committees were constituted as follows:—

In Sweden, Prof. Richard Akerman; in Germany, by the authority of the minister of public works, the execution of the analyses has been entrusted to the Konigliche Chemisch Technischen Versuchungsanstalt, in Berlin; in France, Mons. Ferd. Gautier; in England, the British Association for the Advancement of Science; in America, a joint committee from members of the University of Michigan and of the American Society of Civil Engineers.

This latter body appointed a committee of seven analysts as follows: — Andrew A Blair, Philadelphia, Pa.; Regis Chauvenet, Golden, Colorado; Thomas M. Drown, Boston, Mass.; Charles B. Dudley, Altoona, Pa.; John W. Langley, Cleveland, Ohio; Albert B. Prescott, Ann Arbor, Mich.; P. W. Shimer, Easton, Pa.

The material for analysis at first consisted of four samples of steel prepared in this country. To this was subsequently added a fifth standard selected in England by the Committee for that country.

Reports of progress have been made by the English Committee in the reports of the British Association for the Advancement of Science, volumes for 1888, 1889, 1890, 1891, 1892, the last one particularly containing a full account of the work on the four original standards.

In the United States the attention of the Committee was early drawn to discrepancies caused by different methods of analysis. They therefore prepared a set of supplementary samples known as the experimental standards and to be used only in reviewing methods of analysis. A full report of their work in this line will be found in the Transactions of the American Institute of Mining Engineers, volume xix., 1890, and a brief one in volume xx.

The Swedish Committee through Professor Akerman has made a report which will be given shortly.

The outcome of the American Committee's work on the modes of determining carbon resulted in calling attention to important errors likely to occur when using double

* Read before the World's Congress of Chemists, August 22, 1893. From the *Journal of the American Chemical Society*, xv., [No. 8, 1893.

chloride of copper and ammonium as a solvent for the steel owing to the great difficulty of obtaining this salt free from pyridin and other tarry products. They recommend substituting chloride of potassium for chloride of ammonium, which is found to be a complete remedy. They also found that contrary to the usual practice this solvent must not be neutral, but must be rendered strongly acid with from 5 to 10 per cent of its volume of strong hydrochloric acid.

They also call attention to the great tendency which chlorine compounds have to pass out of the combustion apparatus and to lodge in the absorption train, thus increasing the apparent weight of carbonic acid, and they give methods for arresting it.

During the past year this Committee has continued its work. The communication from Professor Drown given below enumerates very fully the precautions necessary and some inevitable causes of variation in carbon determinations.

Massachusetts Institute of Technology,
Boston, July 29, 1893.

Prof. JOHN W. LANGLEY, *Chairman, Committee on International Standards for the Analysis of Iron and Steel.*

DEAR SIR,—I give you herewith the results of my determinations of the carbon in the experimental steel standard. The sample examined was marked "hammered."

The amount of carbon found in six consecutive analyses was :—

Per cent.

1·050	1·057	1·054	1·030	1·054	1·053

These results were all obtained by precisely the same process and method of manipulation. The agreement is satisfactory with the exception of the fourth. I know of no reason why this result should have been lower than the others. The average of the six determinations is 1·0497. If the fourth determination is omitted, which I think it reasonable to do, the average of the remaining five determininations is 1·0536 per cent.

The process used was as follows :—Three grms. of the steel were treated with 200 c.c. of a solution of copper-potassium chloride (300 grms. to the litre) and 15 c.c. of hydrochloric acid (sp. gr. 1·2). After complete solution of the iron the carbon was filtered off on an asbestos lined platinum boat, thoroughly washed with hydrochloric acid, and then with water until the washings gave no reaction with silver nitrate. After drying, the boat was put into a porcelain tube and the carbon burned in a current of oxygen.

The oxygen used was passed over red hot copper oxide, then through caustic potash, then over calcium chloride before it entered the porcelain tube. The tube contained at its farther end several inches of copper oxide and a coil of metallic silver, which were heated to redness before the carbon was ignited.

The gases on leaving the porcelain tube were passed, first, through a small bulb tube containing an acid solution of ferrous sulphate, then over andydrous copper sulphate on pumice, and finally over calcium chloride before entering the potash bulb. The latter was provided with a small extension tube containing calcium chloride.

Before beginning each combustion two or three blank combustions were made to see that there was no source of error in the apparatus itself. The oxygen was swept out with air (free from moisture and carbonic acid) and the potash bulbs were closed with rubber tubing plugged with capillary glass tubes.

The silver coil, ferrous sulphate, and anhydrous copper sulphate were all used for the purpose of absorbing hydrochloric acid or chlorine. In Mr. P. W. Shimer's communication on this subject he calls attention to the fact that absorbents of hydrochloric acid are unnecessary if the acid is entirely washed out in the original filtration, an operation which would seem to be not at all difficult. I have long held the same view as Mr. Shimer, and yet I am compelled to admit that better agreeing results can be regularly and consecutively obtained if all possible precautions are taken at the time of the combustion against the entrance of chlorine or hydrochloric acid into the potash bulbs.

I am indebted to Dr. C. B. Dudley for the suggestion of the use of ferrous sulphate, and I think it a valuable addition to the process. The solution is made by adding concentrated sulphuric acid to a saturated solution of ferrous sulphate until the latter begins to crystallise out.

A series of determinations made in all respects like those given above, except that this small bulb of ferrous sulphate was not inserted, gave the following results:—

Per cent.

1·073	1·080	1·051	1·051	1·037	1·040	1·049	1·069

There are three abnormally high results in this series, which do not appear in the series in which the ferrous sulphate was used.

In the course of this study I have made several hundred blank combustions to determine what errors might be introduced in the apparatus and manipulation. On some days there would be a constant gain in weight in the potash bulbs; on other days, a constant loss; and, again, at other times, the bulbs would not change in weight, in spite of the fact that the conditions of the experiments as to time, quantities of oxygen and air passed, and arrangement of apparatus were the same. On moist days, as every chemist of experience has observed, it is almost impossible to get a satisfactory weight of the potash bulbs, and it is also well known that differences of temperature between laboratory and weighing room must always be taken into consideration. The very least error, plus or minus, which one must count upon in the final weight of carbonic acid is, I think, 0·0003 grm. This cannot be thought large when one considers the great weight of the bulbs, the large amount of oxygen and air (one or two litres) passing through them, the large surface of glass exposed, and the fluctuating conditions of humidity and temperature in the laboratory and weighing room. And yet this three-tenths of a milligrm. amounts to 0·003 per cent of the carbon when 3 grms. of steel are used for the analysis. It seems to me that a variation plus or minus of 0·005 per cent on carbon in steel is the very least that should be allowed in view of the many sources of error inherent in the combustion process as now generally used. And I am inclined to think that it would be very seldom that the variation on ten consecutive determinations would fall within this limit, even with chemists of experience in this line of work.

I have satisfied myself by many experiments that a small extension-tube filled with very small fragments of calcium chloride attached to the potash bulbs is entirely adequate to collect any moisture that may be carried over from the potash solution, and that the latter does not allow any carbonic acid to pass through. The use of solid caustic potash in the extension-tube is therefore unnecessary. Neither have I found any advantage in the addition of a drop or two of water in the bulb of the calcium chloride tube to moisten the air after it has passed the anhydrous copper sulphate.

In addition to the work above given, I have made a large number of determinations of the carbon in the experimental standard under different conditions. Some of the results thus obtained it may be worth while to record. A determination made in the same series as those first given, and in precisely the same manner, except that copper-ammonium chloride was used instead of the potassium salt, gave the per cent of carbon as 1·053. This would indicate that the ammonium salt can be safely used when free from carbon.* That cupric chloride acidified

* This copper-ammonium chloride was obtained from Messrs. Baker and Adamson, Easton, Pa.

with hydrochloric acid can be used for the solution of the iron has already been shown by other members of the Committee. I have made several experiments in this direction with the view of using this method exclusively, and thus avoid the necessity of using a crystallised double salt of copper. Cupric chloride acidified with 20 per cent of strong hydrochloric acid dissolves iron with reasonable promptness, and gives good results. The addition of 40 per cent of hydrochloric acid is apt to cause loss of carbon. But hydrochloric acid is not as good a solvent of cuprous chloride as the alkaline chlorides.

It seemed obvious that the addition of potassium or sodium chloride to the acidified copper solution would give as good results as a solution of copper-potassium chloride. Several determinations made in this way gave fairly good results. Copper oxide, containing some metallic copper, was dissolved in hydrochloric acid, chlorine gas was passed into the solution to oxidise the cuprous chloride, and the solution was then evaporated to small bulk to expel the free chlorine; it contained some free acid. The amount of copper in this solution was determined by the battery in order that the proper amount should be used in dissolving the steel. Three grms. of steel were treated with an amount of this solution which contained 12 grms. of copper, 15 c.c. of hydrochloric acid (sp. gr. 1·2), and 60 c.c. of a solution of common salt containing 320 grms. to the litre. The steel dissolved readily. The filtration of the carbon and the combustion were made precisely as above described with all the precaution for the interception of chlorine and hydrochloric acid. The results obtained for the carbon in three experiments were:—

Per cent.	Per cent.	Per cent.	Average per cent.
1·055	1·043	1·059	1·052

A similar experiment, using potassium chloride instead of sodium chloride, gave 1·051 per cent carbon.

I have also made large number of experiments with silver sulphate as a solvent for the steel, but I did not obtain any satisfactory results in this way.

I take pleasure in acknowledging my great indebtedness to Mr. Wm. S. Davenport, instructor in analytical chemistry in the Massachusetts Institute of Technology, for the analytical work of this investigation, and for many valuable suggestions regarding the processes employed.

THOMAS M. DROWN.

The original four standards have now been analysed in three countries with the following result.

The English Committee give as the mean of their determinations:—

English Committee.

	Standard No. 1.	Standard No. 2.	Standard No. 3.	Standard No. 4.
Carbon	1·414	0·816	0·476	0·151
Silicon	0·263	0·191	0·141	0·008
Sulphur	0·006	0·007	0·008	0·039
Phosphorus ..	0·018	0·014	0·021	0·178
Manganese ..	0·259	0·141	0·145	0·130

The Swedish Committee, through Professor Åkerman, give their means as:—

Swedish Committee.

	Standard No. 1.	Standard No. 2.	Standard No. 3.	Standard No. 4.
Carbon	1·45	0·84	0·50	0·17
Silicon	0·257	0·185	0·15	0·015
Sulphur	0·008	0·004	0·006	0·048
Phosphorus ..	0·022	0·015	0·021	0·102
Manganese ..	0·282	0·145	0·17	0·13

The American members have not held a joint meeting this year, and there are one or two analysts who have not completed their work, so that the averages given below may suffer some small modification in the future.

American Committee.

	Standard No. 1.	Standard No. 2.	Standard No. 3.	Standard No. 4.
Carbon	1·44	0·807	0·452	0·16
Silicon	0·270	0·202	0·152	0·015
Sulphur	0·004	0·004	0·004	0·038
Phosphorus ..	0·016	0·010	0·015	0·088
Manganese ..	0·254	0·124	0·140	0·098

The German Committee has devoted much attention to the study of methods of analysis in connection with the international standards, but has not yet announced its results. The French Committee has made no report.

THE PURIFICATION OF WATER, WITH SPECIAL REFERENCE TO BOILER FEED WATERS AND SCALE PREVENTION.*

By C. A. DOREMUS.

PROF. VIVIAN B. LEWES, of the British Royal Naval College, has epitomised in two papers read before the Institution of Naval Architects in 1889 and 1891 a series of the most highly interesting and instructive analyses and experiments on incrustations in marine boilers and their causes to be found in the literature relating to scale formation (CHEMICAL NEWS, lix., 222, and lxiii., 191). A careful study for some years of a great variety of boiler feed waters from all sections of the country has convinced me that many points brought forward by Professor Lewes are so generally applicable that they cannot be overlooked by the chemist who attempts to rectify the serious troubles arising from these sources.

The following quotations are typical:—"The presence of calcium sulphate exercises a very marked influence upon the condition and physical properties of the incrustation as under the conditions in which it is formed in a boiler it separates in a crystalline form and binds the deposit into a hard mass, an action which is also aided by the presence of magnesium hydrate." When calcium sulphate is deposited from sea water in a boiler it comes down in small crystals containing two molecules of calcium sulphate and one of water; whilst after deposition in the boiler and in contact with the heated plates and tubes, it undergoes a further change of crystalline form, and becomes "anhydrite, which is pure calcium sulphate free from water of crystallisation, and it this change in crystalline form which binds deposits containing it into such a hard mass."

In many carbonated waters the calcium carbonate also forms upon the heated surface as a crystalline coating, even though the quantity in solution is trivial. Thus in a Croton water which carries but a grain or two per gallon a scale forms on all heated surfaces, tubes as well as crown sheets, which is distinctly crystalline. The massive concretions often found in feed water heaters are crystalline in structure and firmly adherent to the hot tubes or surfaces. It is very easy to show this by a simple experiment. Place a carbonated lime water in a beaker. Raise it to boiling by steam delivered into it by a glass tube. The latter will become coated with an adherent crystalline layer of calcium carbonate. With gypsum water the incrustation does not form so readily since calcium sulphate is soluble to some extent in boiling water, and thorough precipitation not taking place before 140° to 150° C., a state of affairs reached in practice in boilers, where the calcium sulphate then separates in a

* Read before the World's Congress of Chemists, August 25, 1893.

crystalline form and attaches itself to the rough heated metal.

In a paper read at the Newport meeting I called attention to the use of sodium fluoride as an agent hitherto overlooked in water purification. Since then I have had opportunities to get the results of its use in several lines of work, but the present paper will be restricted to the service this substance renders in scale prevention. Starting with the idea that is so prevalent, that successful treatment of feed waters should be accomplished by such chemical or mechanical, or combined chemical and mechanical, treatment, that the incrusting salts should be removed previous to the water entering the boiler, it was soon seen that this theoretical ideal was not practicable. There are many waters which yield an incrustation, whose proportion of lime and magnesium salts is so small that precipitation cannot be effected either by the use of feed water heaters or of chemicals. Yet such waters yield a crystalline scale, and often a scale containing magnesium hydrate. Surface condensers are frequently leaky, and many marine boilers starting with good water acquire scale from this cause. Manifestly such waters can only be treated by chemical means in the course of concentration in the boilers. From these almost soft waters we pass by upward grade to the excessively hard, which can be purified in some measure merely by heating or by chemicals. Since, however, calcium sulphate is not completely precipitated at 100° C., feed water heaters do not remove it thoroughly enough to prevent scale, and where waters have a permanent as well as temporary hardness due to magnesium salts these are not eliminated. When lime, soda ash, or caustic soda, or a combination of any of these is made use of, it is difficult to regulate the amount required to effect so complete a precipitation that no scale will form and the trouble attendant on this style of purification is so great that in many cases it has been abandoned. Water softened by lime and soda ash or treated by soda ash or caustic, will generally possess an alkaline reaction, and is for some purposes therefore unserviceable. The chemical treatment frequently causes the lime salts to separate in crystalline form, large masses of great thickness being formed.

In one instance the feed pipe for a battery of boilers, though five inches in diameter, became so incrusted that a one-inch bar could not be thrust through it. The water had been treated with soda ash and afterwards filtered.

At an artificial ice factory using hard well water the sand of the filter became hard as stone from the calcium carbonate which crystalised upon it even after the water had been treated with soda ash and heated to soften it.

The cost of chemical treatment is often a bar to its employment quite aside from the expense of accessory apparatus, as settling tanks, filters, &c., since to be effective at least the theoretical quantity of precipitant must be used, with soda ash two or three times this quantity.

When sodium fluoride is added to water containing even a very moderate proportion of lime or magnesium salts a precipitate forms at once. When added in quantity sufficient to unite with all of the calcium and magnesium to form fluorides of these metals, and the water is then boiled down, the precipitate retains its amorphous character. Viewed through the microscope, it has always been found powdery and rounded. This circumstance together with other considerations has led to the employment of sodium fluoride in the direction of scale prevention, and it is pleasant to be able to record that today it is in successful operation in nearly every section of the country.

It is not an uncommon practice abroad (L. Vignon, *Bull. Soc. Chim.*, iii., 2, p. 596) to employ sodium carbonate directly in the boiler, transforming the calcium sulphate to carbonate. The conversion not only of the sulphate of calcium but all magnesium salts to pulverulent fluorides therefore seemed possible and has proved practicable. Calcium fluoride has a molecular weight about 25 per cent less than either calcium carbonate or sulphate or an equivalent quantity of phosphate, and therefore the precipitate or sludge formed through its use is much more manageable and removable by blowing down the boilers.

At first it was deemed necessary to determine the total calcium and magnesium of the water often to make a sufficiently complete analysis to determine the salts held in solution and to calculate from these data the quantity of sodium fluoride necessary to transform the calcium and magnesium to fluorides.

Carefully made tests have shown, however, that in the greater number of instances a quantity of sodium fluoride one-quarter of this theoretical amount will, if fed continuously, prevent the formation of scale and leave the interior surface of the boiler so smooth that one chief cause of crystals attaching themselves is done away with.

The various types of water from New York to Albany and from there through the salt district to the lakes at Buffalo are now under this treatment with entirely satisfactory results. The employment of so small an amount of the chemical naturally reduces the cost of purification, while the ease of handling pleases the engineer.

More than once it has happened that the boilers were heavily incrusted when the use of the fluoride was begun. The old scale was found to loosen rapidly, falling off in some cases by the bucket full. In others it was rotted and softened so that on the first cleaning it was easily scraped off.

A specimen of highly silicated scale is presented to show how a chemical transformation with the formation of fluoride has resulted from the continued action of small quantities of sodium fluoride added to the feed water. When once thoroughly cleaned to the metal new scale does not form in such instances.

Live steam is so frequently used now in our large manufacturing establishments for cooking, boiling, &c., and so much condensed steam is used to furnish distilled water, especially in artificial ice manufacture, that a method of treating boiler water in such a way as to furnish pure untainted steam is exceedingly desirable. Since sodium fluoride completes its work without rendering the water alkaline, the steam from water thus treated has proved most excellent for such purposes.

It is beyond the province of this article to enter more fully into these details.—*Journal of the American Chemical Society*, Nov., 1893.

ON THE VOLUMETRIC SEPARATION AND DETERMINATION OF LEAD.

By MM. LINDEMANN and MOTTEN.

Determination of Lead in Galena.—The ore is disintegrated in the following manner:—From 500 m.grms. to 1 grm. of the pulverised ore are placed in an agate mortar. A few drops of a solution of chloride of lime are added, and the pulverisation is continued until a kind of mud is obtained. The ore is thus brought into a state of subdivision which it is difficult to reach by dry pulverising. A few more drops of the solution are added, and the trituration is continued until some 40 c.c. of the solution have been employed. Lastly, we add from 30 to 40 c.c. of the solution and chloride of lime by small quantities at once, and still continuing to triturate. We then add, little by little, hydrochloric acid diluted to 50 per cent, stirring until the oxides formed are dissolved. The slow development of chlorine thus effected promotes the oxidation of the last portions of sulphur. The liquid obtained is poured into a beaker, the washing water is added, and the whole is submitted to a gentle heat.

If the operation is well conducted the oxidation of the

ore is complete. The traces of sulphide which have escaped the action of the chloride of lime are oxidised by the action of chlorine and of heat. If any sulphide still remains unattacked it is sufficient to add a little chloride of lime, and to carry on the action at a moderate temperature.

In the case of galena free from other heavy metals we add to the solution obtained, containing the gangue, a quantity of chloride of lime to precipitate all the lead in the state of peroxide. This precipitation is effected at a temperature of from 60 to 70°. The liquid is allowed to subside, and when cold the precipitate is washed by decantation, bringing it upon the filter as little as possible. The nature of the precipitate is adapted for washing by decantation. The precipitate is washed until the filtrate no longer gives the reaction of chlorine.

Into the beaker containing the precipitate there is poured an excess of potassium iodide (25 c.c. of a 50 per cent solution are generally sufficient). The small quantity of peroxide in the filter is driven into the beaker by means of the washing-bottle. The hydrochloric acid necessary for the reaction (about 30 c.c. HCl at 20 per cent) is poured upon the filter in order to dissolve any adhering traces of peroxide, and the liquid is received in the beaker. As mere traces of the precipitate remain upon the filter there is no fear, with an acid of this strength, of any loss of chlorine. We wash the filter and the sides of the beaker, so as to make up a volume of 150 to 200 c.c., and after stirring for a few moments the reaction is complete, and we proceed to the titration of the iodine set at liberty. In proportion as the thiosulphate is added we see the brown colour of the solution of iodine in potassium iodide by degrees give place to the yellow colour of lead iodide. The end of the operation is indicated when a drop of the liquid placed on a leaf of ordinary white writing-paper no longer gives a blue colour. The presence of lead iodide does not interfere with the final reaction.

Separations.—When galena contains foreign metals such as iron or copper it is necessary to eliminate them, as their chlorides would liberate iodine. After various trials we adopted the use of hydrogen sulphide as the most accurate and expeditious means. The use of H_2S further enables us to eliminate all the metals of the iron group which may accompany the ore.

I. *Galena free from Copper.*

If the ore is free from copper—the most general case—we heat the liquid obtained by the action of chloride of lime upon the galena until the chlorine is expelled; we dilute with water, and pass in a current of H_2S. The lead sulphide is washed by decantation, with the precautions indicated above for the peroxide. The lead sulphide which has been carried upon the filter is treated upon it (after perforating the paper) with chloride of lime rendered strongly acid, and the liquid is collected in the beaker containing the precipitate. The lead oxide formed is dissolved upon the filter in HCl at 20 per cent, and washed with hot water. We pour into the beaker a sufficient quantity of chloride of lime, and heat slightly, and the transformation of the lead sulphide and chloride into peroxide ensues immediately.

II. *Galena containing Copper.*

If the ore contains copper the lead sulphide obtained by the action of H_2S is washed by decantation as above, and then treated with a little potassium cyanide to dissolve the copper sulphide. We leave the liquid in contact for a few moments, pour it upon the filter in order to submit the lead sulphide which has been carried over to the action of the potassium cyanide. We wash, and continue the analysis as above.

Standardising the Thiosulphate.

We dissolve, in 1000 c.c. of water, 6·401 grms. of iodine with potassium iodide, and about 24 grms. of sodium thiosulphate in another litre of water. Hence 1 c.c. solution of thiosulphate = 10·04 m.grms. of lead.

The standard of the solution of thiosulphate having been thus fixed hy iodine, we determined it on substituting a lead-salt for the iodine. We selected lead sulphate, which is easily obtained pure. We found as a mean 1 c.c. of thiosulphate = 10·012 Pb. — *Société Chimique de Paris.*

THE SEPARATION OF LEAD AND COPPER BY MEANS OF HYDROGEN PEROXIDE IN AN ALKALINE SOLUTION.

By P. JANNASCH and J. LESINSKY.

As the initial point for our separations we used lead nitrate, pure metallic copper, and copper sulphate. For effecting the separation about 0·5 grm. lead nitrate and 0·3 grm. metallic copper were dissolved in 50 c.c. water and 10 c.c. strong nitric acid, in a capacious porcelain capsule with a handle, and then mixed in the cold with a mixture of 60 c.c. of hydrogen peroxide at 2 per cent at least, and 20 c.c. concentrated ammonia. To the yellowish-brown precipitate of hydrated lead peroxide we lastly added 5 c.c. of a saturated solution of ammonium carbonate, in order to be certain that the last traces of lead are precipitated and collected, the precipitate on a filter of moderate size. This precipitate is washed four or five times,—first in the cold, with a mixture of 1 vol. hydrogen peroxide, 6 to 8 vols. strong ammonia, until the blue colour is no longer perceptible in the filter; then with hot dilute ammonia at about 60° to 80° (1 vol. strong ammonia to 8 vols. water), and finally completely washed with water of the same temperature. We were not able to obtain the hydrated lead peroxide perfectly free from copper by merely washing with cold ammonia and water, so that the determinations were on the average 0·5 per cent too high. Our fear that lead peroxide might prove slightly soluble in hot water and ammonia fortunately proved to be unfounded. In filtering off the lead precipitate it must be noted that minute particles sometimes pass through the filter, which necessitates a re-filtration of the first portions of the filtrate. The washed lead precipitate is then dried in the air-bath, then incinerated in a porcelain crucible along with the filter; the residual oxide is treated with dilute nitric acid to effect complete solution, and the liquid thus obtained is evaporated to dryness on the water-bath. The nitrate thus obtained had a pure white colour. The covered crucible is then placed in an open air-bath, and heated for at least half an hour in order to render the lead nitrate perfectly anhydrous. When absolutely dry it is heated over a small flame until no vapours escape, and it ceases to smell of nitric acid. Finally it is heated rather strongly, to decompose all the nitrate (heating until the weight becomes constant).

The deep blue copper filtrate is strongly concentrated to expel all ammonia, a corresponding quantity of water is added, and 10 c.c. concentrated sulphuric acid. It is concentrated anew, and allowed to stand upon the water-bath until all nitric acid has been driven off. About 100 c.c. of water are added, any deposit of silica is filtered off, the filtrate is diluted to 350 or 400 c.c., heated to ebullition, and sulphuretted hydrogen gas is passed into the hot liquid until the pure black copper sulphide is completely deposited. This precipitate is filtered off, washed with hot sulphuretted hydrogen water, immediately incinerated along with the filter; when cold it is well crushed in the porcelain crucible with a stout glass rod, pulverised, and finally gently heated in a current of air which has been passed through a saturated solution of ammonium carbonate, so that volatile ammonium sulphate may be formed from the copper sulphate present,

whilst the watery vapours effect the oxidation of the metallic copper simultaneously formed during the incineration of the copper sulphide. This method in experienced hands gives perfectly correct results. It requires, however, a careful regulation of the temperature, as on heating too strongly there occurs a partial reduction to metallic copper. It is therefore more certain and convenient to cover the mixture of copper oxide, copper sulphate, and metallic copper with a concentrated solution of ammonium carbonate in the crucible, to evaporate to dryness and to heat the dry residue in a current of oxygen, at first gently and then more strongly until the weight is constant.

In the course of our operations we made the important observation that if we used for the precipitation of the lead an abundant excess of hydrogen peroxide, the reddish brown flocculent precipitate was quickly converted into white nacreous leaflets, perfectly insoluble in water, cold or hot, and in dilute ammonia.—*Berichte der Deutsch. Gesell.*, xxvi., 2331.

THE USE OF QUINONE-OXIMES IN STEAM STYLES.

By M. PRUD'HOMME.

Dinitroresorcine and in general the quinone-oximes can be easily fixed as dyes with mordants of iron, copper, nickel, cobalt, &c., that is with oxides of the metals which may occur in various states of oxidation. On the contrary they do not form lakes with alumina.

The quinone-oximes react directly with the salts of the metals enumerated, yielding coloured insoluble lakes. This property is opposed to their use in steam-colours, that is to say in colours which contain all the elements necessary for the formation of a lake (colouring-matter and mordant) and merely require to undergo the operation of steaming.

The author has observed that the solutions of potassium ferro- and ferri-cyanide if heated to ebullition with dinitroresorcine evolve hydrocyanic acid, and deposit a green precipitate in which the ordinary reagents for iron cannot detect this metal. This migration of the iron from a compound in which its properties are masked to another in which they are also masked is a very curious phenomenon. Practically it permits of the use of the quinone-oximes in steam styles. A colour made in the cold with dinitroresorcine and red prussiate yields on steaming a very deep green, analogous to that of cœruleine fast as against light and soaping. Red prussiate, more advantageous than yellow prussiate, is used in equal weights with dinitroresorcine at 50 per cent. The addition of a small quantity of chromium acetate, probably occasioning the formation of Havraneck green, increases the intensity of the same. It is the same on printing cloth prepared in oil for Turkey reds.—*Bull. Soc. Industrielle de Mulhouse.*

THE ACTION EXERTED BY CERTAIN METALS UPON THE ACID SOLUTIONS OF THEIR CHLORIDES.

By A. DITTE and R. METZNER.

If we plunge a slip of tin into a concentrated hydrochloric solution of stannous chloride covered with a layer of water we know that crystals of tin are quickly formed near the plane of contact. At first sight we are led to ascribe their production to electrolysis. If, in fact, we consider the system constituted by the bar of tin and the two liquids it amounts to two identical electrodes plunging into different solutions, separated by their plane of contact, and we perceive as sources of electromotive force on the one hand the contact of the tin with the acid liquor which dissolves it, and on the other the contact of the liquids by the common surface at which the hydrochloric acid is diffused in the water, with a decided liberation of heat and the production of a current passing from the acid liquor to the water through the plane of separation.

Let us admit for the moment that the sum of these electric actions is sufficient to electrolyse the dissolved stannous chloride, and we can easily render account of the peculiar features presented by the experiment.

A plate of tin plunged into the hydrochloric solution of stannous chloride does not give rise to the formation of crystals, but they appear as soon as we pour upon the surface a layer of water. This water, however little mixing with the subjacent liquid, rapidly becomes conductive enough to transmit the current, and this weak solution of tin salt behaves as an electrolyte. If instead of a thin layer of water we deposit a thick stratum it is at first in the neighbourhood of the plane of contact that the water mixed with tin salt is the most conductive, and allows the current to pass most easily. It is near this plane that the crystals appear. As the diffusion is effected the upper liquid becomes conductive at distances greater and greater from the plane of separation, and the electrolysis is effected over a space more and more extensive; but the upper liquid may be considered as formed of super-imposed surfaces less and less conductive. The current which traverses it will be continuously enfeebled, and the results obtained are those yielded by the electrolysis of the salt of tin in solutions more and more dilute by weaker and weaker currents. Setting out from the plane of separation the crystals of tin decrease in size. If we examine them at higher points in the upper liquid they are gradually transformed into a spongy layer, grey and dull, which at still higher levels is reduced to a black dust of tin in a very fine state of division.

In fine, above the surface of separation, the bar of tin plays merely the part of a negative electrode, and may be replaced by any other conductor, *e.g.*, a platinum wire, the point of junction of which, with the tin, is a little above the plane of separation. The deposit of crystalline tin is made upon the platinum quite as well as upon the bar of tin in the former experiment and in the same manner. Further, we may cause the crystals to appear at a given point of the bar. For this purpose it is sufficient to render the upper liquid conductive at this point, and to introduce there salt of tin. This is effected by touching the points of the platinum rod with a pipette drawn out very fine, containing a hydrochloric solution of stannous chloride. We see almost immediately appear at this point crystals the formation of which follows the descending movement of the liquid drop along the platinum. If the layer of water is very deep, and if we deposit a small quantity of tin salt far from the plane of contact, we obtain in place of crystals the black pulverulent deposit given by a very weak current in a dilute solution. If, on the contrary, the composition of the upper layer is everywhere alike the crystals appear at once all the length of the conductor, and have everywhere almost the same appearance.

To explain these phenomena we have admitted that they are the result of an electrolysis by a current due to two causes; on the one hand, the solution of tin in the hydrochloric acid, and on the other the diffusion of the hydrochloric acid in the water through the plane of contact. At first we have certainly a phenomenon of electrolysis, for if we replace the bar of tin by a system composed of two bars, the one placed as a continuation of the other but separated by an insulating portion crossing the plane of contact, we observe nothing until, thanks to the progress of the diffusion, the base of the upper bar and the top of the lower bar are immersed in conductive liquids of different composition which bring them into communica-

tion. We then see crystals appear on the base and the summit above-mentioned.

Secondly, the attack of the tin by the hydrochloric acid and the resulting current are indispensable for the production of crystals. We do not observe them if we form the lower stratum of a solution of stannous crystals, concentrated but not acid.

Thirdly, as we may easily ascertain, this current is of itself insufficient for the electrolysis of the dissolved salt of tin. The phenomenon of the deposition of crystals does not occur unless we cause to intervene the electromotive force which takes its rise at the contact of the two liquids and their diffusion one through the other. But, on the other hand, this force alone is not sufficient. A couple formed by a porous vessel full of concentrated hydrochloric acid holding stannous chloride in solution, a vessel of water acidulated with hydrochloric acid and plates of platinum immersed in the two liquids separated by the porous system, does not effect the electrolysis of the stannous chloride.

If for the stannous chloride and the tin we substitute cadmium chloride and cadmium, a metal not readily attacked by a very dilute solution of hydrochloric acid, we obtain phenomena quite similar to those above described and crystals of cadmium. With a metal such as zinc capable of decomposing water, and consequently of being dissolved by the most dilute hydrochloric acid, nothing analogous ensues. The crystals would be attacked by a liquid too dilute to be conductive. A substance like nickel, which in the acid is quickly covered with a protective layer of hydrogen, and consequently does no longer touch the liquid, and is not dissolved in it, does not give rise to a crop of crystals.

It is, *a fortiori*, the same with such metals as bismuth and antimony, upon which hydrochloric acid has no action.—*Comptes Rendus*, cxvii., p. 691.

ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

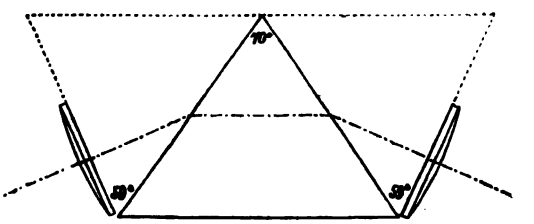
(Continued from p. 300).

The exhaustion of the air was effected in from ten to fifteen minutes. The pressure sank from below that of a mercurial column of 1 m.m. Afterwards there certainly occurs a small increase of pressure due to the air adhering to the inner sides of the apparatus and in the pores of the brass case. Where this change of pressure interfered the exhaustion lasted longer, requiring hours, and though I was certain that there was no fluctuation of pressure during the exposure, I was not able to procure evidence of this for a long time afterwards. I mean that the barometer test of the air-pump in comparison with the cathetometer is useless; but changes are shown in the most striking manner in the stratifications of the Geissler tube. Such small fluctuations were unimportant in the present proofs in as far as they affected the absorption. It could not be otherwise with their influence upon the optical power of the apparatus—a question which, as I shall at once show, became important for the proofs.

Even the first proof, with the exhausted apparatus, showed how favourable was the action of a decrease of the stratum of the air. The spectrum of tungsten now extended beyond the wave-length 185·2 $\mu\mu$, one-half further into the ultra-violet than formerly. I effected more in one minute than previously in fifteen minutes. The two components of the aluminium line No. 32 appear in these proofs at a distance from each other of 0·5 m.m. With ½ metre of air, and an exposure of fifteen minutes, the tungsten spectrum can be traced 2·5 m.m. towards the more refrangible side, but with 1 c.m. of air and an exposure of one and a half minutes it can be followed for 4 m.m. Hence in my earlier proofs the air had acted as a very considerable obstacle. The want of transparency of a thicker stratum of air was shown still more distinctly in photographing the aluminium spectrum. In thirty seconds there appeared at a distance of 6 m.m. from No. 32 (consequently where no action of light had ever been detected) the first traces of a group of lines with which, after fifteen minutes, with a slight increase of their intensity, there were associated three more strongly refracted lines. The most refrangible of these lines lies 9 m.m. from No. 32. All attempts to demonstrate the presence of still more refrangible lines proved unsuccessful. This was the result concerning the original object of the vacuum proofs, the absorption of the rays in the air.

It was different with the applicability of the apparatus for the ultimate purpose of my work—the exploration of the region of the smallest wave lengths. It resulted plainly from all my vacuum proofs that an apparatus containing air could no longer be used. Without the vacuum every further improvement of my means of observation must remain non-effective.

But the vacuum alone was not sufficient. Without perfect sharpness, the spectra, in consequence of their small length (to which I was compelled by the constructive difficulties of the apparatus), were worthless. I must lay an equally great weight upon clear definition. And in this point my early vacuum proofs were altogether defective. All their lines appeared blurred. Nowhere appeared the sharpness to which I had been accustomed in former proofs with the same prism and the same lenses. Without ascertaining the cause of this defect, any further progress in my research was cut off.



There were two essential points in which the exhausted apparatus differed from that containing air. In the vacuum refraction and dispersion were effected by the fluor-spar prism alone. But in the apparatus containing air they were effected by the same prism and, in addition, by two air prisms which enclosed the former in a reversed direction symmetrically after the manner of Rutherford prisms and probably were not without influence upon the refraction and length of the spectrum.

(To be continued).

* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

NOTES ON THE OXIDES CONTAINED IN CERITE, SAMARSKITE, GADOLINITE, AND FERGUSONITE.*

By WOLCOTT GIBBS, M.D.,
Rumford Professor (Emeritus) in Harvard University.

In the present paper I have brought forward a number of observations and analyses which I hope will be of service to those who are engaged in the study of the rarer earths. The subject is one of such extreme difficulty that even the results of an imperfect study may have value.

For the material which I have employed I have been

* *American Chemical Journal*, xv., No. 7.

chiefly indebted to Dr. Waldron Shapleigh, Chemist to the Welsbach Incandescent Light Company, by whom I have been liberally supplied with various preparations in a state of considerable purity. I have also to make my acknowledgments to Prof. Everhart, from whom I have received a considerable quantity of gadolinite from the well-known locality in Llano County, Texas. The material given me by Dr. Shapleigh consisted in part of beautiful crystalline double nitrates of the earths and ammonium, and in part of crude oxides. The double nitrates contained only the earths present in cerite, and for the most part only Ce_2O_3, Ln_2O_3, Ps_2O_3, and Nd_2O_3, with very small relative quantities of Y_2O_3, and traces only of other earths. In converting the crude oxides into sulphates it is best to sift the fine powder slowly upon the surface of cold dilute sulphuric acid. The sulphates are then formed at once as fine crystalline powders free from hard lumps. Another method sometimes applicable with advantage consists in mixing the oxides with an excess of ammonic sulphate, and then igniting slowly in porcelain crucibles, which are to be heated in a muffle to low redness until vapours are no longer given off. The sulphates then present a beautiful snow-white soft crystalline powder, and readily form saturated solutions with cold water. In all work with the rare earths, oxalates from their insolubility play a very important part. They may, as all chemists know, be readily converted into sulphates by treatment with sulphuric acid and careful expulsion of the excess of this last by heat. I have found it more convenient to mix the oxalate intimately with an excess of ammonic sulphate and heat carefully in a muffle, as in the last case. The resulting sulphates are perfectly soluble without packing together if sifted upon the surface of cold water. They are also perfectly neutral. The oxalates may also be converted into chlorides by mixing them intimately with ammonic chloride and igniting the mixture in a muffle very gently.

Determinations of mean atomic mass are now always employed in the study of the mixtures of oxides which present themselves in the attempt to effect separations. Very accurate results are obtained by the usual method of converting a weighed quantity of oxides into the equivalent weight of sulphates by treatment with sulphuric acid and subsequent careful ignition. Probably this could be done more conveniently, and in less time, by igniting the oxides in porcelain crucibles in a muffle, after mixing carefully with ammonic sulphate; but upon this point I have made no quantitative experiments.

In all my work I have employed the analysis of the oxalates as convenient and accurate. It is, however, necessary to insist upon several points of detail. In the first place I remark that the preparation of perfectly homogeneous mixtures of the oxalates requires much care. It is best to precipitate by a hot dilute solution of oxalic acid added slowly in small but distinct excess to a hot dilute solution of the mixed chlorides or nitrates. The precipitated oxalates are then to be thoroughly washed by decantation with hot distilled water. This requires in general a large quantity of water, and must be continued until the washings contain no trace of oxalic acid and give no cloudiness with ammonia. Auer von Welsbach's process, which consists in adding a very dilute solution of the nitrates (or chlorides) to a hot dilute solution of oxalic acid, gives the oxalates in a state of very fine subdivision and perfectly free from hard masses. The mixed washings on saturation with ammonia sometimes give a precipitate of oxalates, though in small quantity. These oxalates may be washed and mixed with the main portion. The mass is to be dried upon a water-bath, and then thoroughly mixed in a dry mortar. Only in this manner is it possible to obtain a mass of oxalates sufficiently homogeneous to yield corresponding results when different portions are analysed. The determination of the mean atomic mass in the oxalates prepared as above involves only the determination of the percentages of oxide R_2O_3 and of C_2O_3, the water present being of course without influence. Here I may remark that, as has doubtless been observed by other chemists, the last portions of water require a very high temperature for expulsion. The details of the method which I employ are as follows:—From 0·5 grm. to 1 grm. of the oxalate is to be gently heated until the greater part of the water and carbonic dioxide have been driven off, and then at a full red-heat for fifteen to twenty minutes with a blast-lamp to a constant weight. During ignition the crucible is best placed at an angle, and partly uncovered to permit free access of air. The mixed oxides do not retain a weighable amount of carbonic dioxide. To determine C_2O_3, from 0·3 grm. to 0·4 grm. of the oxalate are to be weighed into a 250-c.c. flask; 20 c.c. of water and 30 c.c. of dilute sulphuric acid, 1:6 by volume, are then to be added, and the flask is to be gently heated upon a sand-bath until the solution is complete, when the hot liquid is to be titrated with carefully standardised permanganate. The following analyses will show the correspondence between the results obtained by the above-described method and those obtained by the sulphate process. In an oxalate from a perfectly colourless nitrate of lanthanum and ammonium sent me by Dr. Shapleigh—

(1)	0·3344 grm.	gave	0·1009 grm.	C_2O_3 =	30·15 per cent.
(2)	0·3274 ,,	,,	0·09895 ,,	C_2O_3 =	30·07 ,,
(3)	0·3726 ,,	,,	0·1120 ,,	C_2O_3 =	30·08 ,,
(4)	0·3485 ,,	,,	0·1050 ,,	C_2O_3 =	30·11 ,,
(5)	0·5931 ,,	,,	0·2706 ,,	R_2O_3 =	45·61 ,,
(6)	0·5977 ,,	,,	0·2728 ,,	R_2O_3 =	45·64 ,,

The means are 30·10 per cent C_2O_3, and 45·625 per cent R_2O_3. The mean atomic mass calculated from the above is 139·70. Dr. Shapleigh found by the sulphate method 139·75, 139·72, 139·67; mean, 139·71.

The necessity of thoroughly mixing the oxalates will appear from the following analyses made with oxalates simply washed and dried:—

(7)	0·3549 grm.	gave	0·1274 grm.	C_2O_3=	35·88 per cent.
(8)	0·3697 ,,	,,	0·1316 ,,	C_2O_3=	35·59 ,,
(9)	0·3807 ,,	,,	0·1382 ,,	C_2O_3=	36·29 ,,
(10)	0·6550 ,,	,,	0·2869 ,,	R_2O_3=	43·79 ,,
(11)	0·6125 ,,	,,	0·2699 ,,	R_2O_3=	44·07 ,,

The same oxalates carefully mixed in a mortar were also analysed for comparison:—

(12)	0·3357 grm.	gave	0·1213 grm.	C_2O_3=	36·16 per cent.
(13)	0·3856 ,,	,,	0·1393 ,,	C_2O_3=	36·13 ,,
(14)	0·6538 ,,	,,	0·2906 ,,	R_2O_3=	44·45 ,,
(15)	0·7074 ,,	,,	0·3145 ,,	R_2O_3=	44·46 ,,

The analyses leave no doubt whatever as to the necessity of carefully mixing the precipitated oxalates. They also show that in determinations of atomic mass by the sulphate method both oxalates and oxides should be well ground up to secure homogeneity. It has been shown that the oxalate and sulphate methods, executed with proper care, give equally accurate results. Each has its advantages, and in this respect there is but little choice. As the study of the rarer earths as now conducted usually depends more or less upon the properties of the double salts which they form with potassic and sodic sulphates, it may be well to call attention to facts not, I believe, noticed in printed papers, though doubtless recognised. The first is that the earths in the double sulphates may be converted directly into oxalates by boiling the sulphates with chlorhydric and oxalic acids, and then diluting with much water. The second fact is that oxalates obtained in this way, as from any alkaline solutions, should always be converted into oxides by ignition. These should then be dissolved in chlorhydric acid, again precipitated by oxalic acid, and the oxalates thoroughly washed.

In determining atomic masses by either the sulphate or oxalate method, the assumption is tacitly made that all the oxides taken for analysis are of the type R_2O_3. This is not true when cerium is present, as in that case a portion at least of this metal is present as CeO_2 after ignition. Higher oxides than R_2O_3 are also present to some extent, at least when praseodymia and neodymia are mixed with ceria, or even when this last oxide is absent. Ceric oxide is not reduced by a full red-heat to cerous oxide, or even by a current of hydrogen, at least in a crucible. The error committed is not, however, large when we consider the cerium as Ce_2O_3 instead of Ce_2O_4, and is still less in the cases of the other oxides. When great accuracy is necessary it may be well to remove the four cerite oxides by means of potassic or sodic sulphate before determining the atomic mass.

In a number of analyses I determined the percentage of oxides by simply igniting the oxalate with a weighed quantity of pure sodic tungstate. This method gives very accurate results, but, as pure sodic tungstate must always be specially prepared in the laboratory, is not to be greatly recommended. Ceric oxide is not reduced to cerous oxide by heating with the tungstate to a red-heat for some time. I may here state that a test for ceria more delicate than that which I gave many years since (PbO_2 and NO_3H) is obtained by employing the oxide of bismuth, Bi_2O_4, in place of plumbic oxide.

With these preliminaries I proceed to special methods of separating the mixed oxides. A series of experiments was first made to determine to what extent differentiation is effected by successive partial precipitations by oxalic acid. The method is of course not new, but, so far as I know, it has not been tested by quantitative analyses, and no attempt has been made to determine the rate of change. The material used in this case was a mixture of sulphates, the sulphate of neodymium being present in largest quantity. Thoric and other oxides in less quantity were also present. The material was obtained from Dr. Shapleigh in the form of oxides. After careful purification the atomic mass of the oxides was first determined:—

(16)	0·5622 grm. gave	0·1715 grm.	$C_2O_3=30·50$	per cent.
(17)	0·4782 ,,	0·1458 ,,	$C_2O_3=30·50$	,,
(18)	0·4355 ,,	0·1326 ,,	$C_2O_3=30·47$	,,
(19)	0·6100 ,,	0·2778 ,,	$R_2O_3=45·55$	,,
(20)	0·6904 ,,	0·3141 ,,	$R_2O_3=45·50$	,,

The analyses give as the atomic mass 137·25. A portion of the oxides was then converted into sulphates, and the number of c.c. of a solution of oxalic acid required for complete precipitation determined by experiment with a sufficiently close approximation. A solution of the sulphates having a very fine rose-red colour was then precipitated in five successive additions of equal volumes of a solution of oxalic acid. After each addition of the acid the resulting oxalate was filtered off and washed. The washings were then added to the filtrate. It will be seen that in this way the bulk of the solution increased before each precipitation after the first. The results are as follows:—

I.

(21)	0·3126 grm. gave	0·0941 grm.	$C_2O_3=30·52$	per cent.
(22)	0·3410 ,,	0·1042 ,,	$C_2O_3=30·54$	,,
(23)	0·5773 ,,	0·2820 ,,	$R_2O_3=48·84$	,,
(24)	0·5856 ,,	0·2855 ,,	$R_2O_3=48·75$	,,

Atomic mass 148·60.

II.

(25)	0·3563 grm. gave	0·1114 grm.	$C_2O_3=31·26$	per cent.
(26)	0·3500 ,,	0·1091 ,,	$C_2O_3=31·20$	,,
(27)	0·6848 ,,	0·3317 ,,	$R_2O_3=48·43$	,,
(28)	0·6664 ,,	0·3223 ,,	$R_2O_3=48·37$	,,

Atomic mass 143·35.

III.

(29)	0·3500 grm. gave	0·1113 grm.	$C_2O_3=31·78$	per cent.
(30)	0·3127 ,,	0·09936 ,,	$C_2O_3=31·77$	,,
(31)	0·6859 ,,	0·3345 ,,	$R_2O_3=48·75$	,,
(32)	0·7087 ,,	0·3447 ,,	$R_2O_3=48·65$	,,

Atomic mass 141·55.

IV.

(33)	0·3350 grm. gave	0·1042 grm.	$C_2O_3=31·12$	per cent.
(34)	0·3410 ,,	0·1060 ,,	$C_2O_3=31·09$	,,
(35)	0·6369 ,,	0·2958 ,,	$R_2O_3=46·44$	,,
(36)	0·6468 ,,	0·3004 ,,	$R_2O_3=46·45$	,,

Atomic mass 137·25.

V.

(37)	0·2042 grm. gave	0·06864 grm.	$C_2O_3=33·62$	per cent.
(38)	0·2031 ,,	0·06828 ,,	$C_2O_3=33·62$	,,
(39)	0·3045 ,,	0·1409 ,,	$R_2O_3=46·26$	,,
(40)	0·3400 ,,	0·1569 ,,	$R_2O_3=46·14$	,,

Atomic mass 124·40.

The filtrate from the last portion of oxalates contained only traces of earths. The analyses show that the earths with the highest atomic masses are precipitated first by oxalic acid. The average rate of decrease of mean atomic mass is five units for each operation, but the rate is by no means uniform. The results prove that precipitated oxalates must be very carefully mixed mechanically before analysis when more than one earth is present. The analyses also show that four-fifths of the earths might have been precipitated at once by oxalic acid if the object had been to obtain yttria with the least outlay of time and labour, the atomic mass of the last fifth being 124·40.

(To be continued).

NOTICES OF BOOKS.

Pigments, Paint, and Painting. A Practical Book for Practical Men. By George Terry. London: C. and F. N. Spon. New York: Spon and Chamberlain. Small 8vo., pp. 392.

The author of this useful work takes a somewhat different scope from other writers on pigments. He enters less fully than do some authorities into the chemical composition of the manufacture of paints, especially of the finer kinds, but he enlarges extensively and ably on white-lead and ultramarine. The destructive action of white-lead, both during manufacture and in its use, is expounded fully and correctly without any unnecessary temporising, but at the same time without the clap-trap exaggerations of a certain portion of the press. Perhaps the only full remedy for the mischief still going on will be the abandonment of white-lead. For this, as for many other evils, the public must look for salvation not to the rhodomontades of the platform and the political press, but to the quiet researches of chemists and physicists.

Mention is here made of an offensive odour evolved in the manufacture of lamp-black, which "occasions head-ache, but is not otherwise injurious to health." We must here submit that frequent exposure to any fumes which occasion head-ache can scarcely fail to be generally injurious to health.

In treating of Prussian blues the author goes back to the preparation of potassium ferrocyanide.

Concerning ultramarine the author makes an important remark which will bear generalising. He says "It is a characteristically English failing to overlook branches of business not dealing with large quantities of staple commodities, and thus many of the smaller but remunerative industries have passed out of our hands." This is one of the causes of our unsatisfactory position as regards the coal-tar colours, which in their earlier state were

made chiefly on a small scale. We cannot, however, agree with the statement here quoted, that "ultramarine is the most beautiful and lasting of all known blue colours." Its destruction by acid vapours is familiar to every one, and its injury by contact with pigments containing lead, &c., is almost equally striking.

The excellence of the Cyprian and Irish umbers is undeniable.

The shortcomings of the Brunswick greens and their sophistications are here recognised.

The development of pigments fit for house painting has been much interfered with by the "contract system." We accidentally overheard part of a conversation between a decorator and a colour-manufacturer. Said the former "Your paints stand too long for us."

Mr. Terry tells us (p. 153) that "vermilion is gradually going out of use; the newer reds, which are *more brilliant in colour*, are gradually displacing it." We wish he had named some of these newer reds. Geranium red, a mercuric iodide, is certainly more brilliant than vermilion, but it is more fugitive as well as more costly.

A fraud, not here mentioned, is the addition to inferior vermilions of eosine red, This fraud is easily detected by washing the sample with dilute alcohol, which dissolves away the eosine and leaves the vermilion shorn of its beauty.

The success of the Chinese in the production of vermilion, ignorant as they are of chemistry and physics, is justly mentioned as an interesting outcome of patience and perseverance.

We find here no mention of the beautiful "mineral lake," a compound of tin and chrome. It closely resembles madder lake in tone, but in permanence it is one of the best of all known pigments.

Concerning the lake colours he says little, and for the lakes of the coal-tar colours he refers the reader to another work.

The preparation of white-lead is discussed and illustrated at length. Zinc white (zinc sulphide) is also ably treated, and so is China clay (Cornish clay). Still we must remember that the use of this valuable mineral as a paint is very small in extent compared with its employment in other manufactures.

The yellow pigments are not treated at great length. The detection of chromates and of orpiment used in sophistication of cadmium yellow is duly expounded. It is, we submit, high time that the use of arsenic in compounding pigments should be severely punished.

There are further chapters on luminous paints, on "vehicles," and dryers. The whole forms a highly useful manual, not only for the manufacturers of pigments, but for painters of every grade, from Royal Academicians down to ordinary house-painters.

Analysis of Milk and Milk Products. By H. Leffmann, M.D., Ph.D., and W. Beam, M.D. Philadelphia: Blakiston, Son, and Co. 1893. 8vo., pp. 89.

We find here a table of the percentage composition of the milk of various animals, including that of the "gamoose," a creature which we certainly do not know under that name. Attention is called to the rapid multiplication of the cholera spirillum if introduced into sterilised milk.

For determining the specific gravity of milk the authors recommend the "lactodensimeter," and, if greater accuracy is required, the Westphal balance, which is much preferable. There is no sufficient caution given as to the fallacious character of specific gravity, by whatever method obtained, for showing the quality of milk. In the determination of total solids the authors take 1 to 2 grms. The Wanklyn method of determining fat is objected to as giving results 0·5 or upwards per cent below the real quantity. The Adams process is approved of, but the authors seem to have a preference for the "lactocrite" method—which is objectionable as it has been patented—and the Leffmann-Beam method, which, like the foregoing, requires machinery, and has also been patented. We must here remark that the patenting of analytical processes cannot be too strongly condemned.

For estimating the nitrogenous matter a modification of the Kjeldahl method is prescribed. Sugar is determined by Soxhlet's process.

The adulterations of milk are considered at some length. There is, in our opinion, no satisfactory evidence that the brains of calves are used in the sophistication of milk. Boric acid, borax, &c., are mentioned as being used as antiseptics, but without the condemnatory decision on their use which K. B. Lehmann has so justly given. Annatto often contains matter which is, to say the least, highly disgusting, and which may introduce disease-germs.

The remarks on the sanitary relations of milk contain views which cannot be accepted.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvii., No. 25, December 18, 1893.

At the Annual Public Session of the Academy M. de Lazase, the President, delivered an Address in which he discussed the question of scientific nomenclature. Here he quoted with deserved approval the dictum of Linnæus that "*Nomina generica sesquipedalia, enunciata difficilia vel nauseosa fugienda sunt.*" As an instance of such names he quotes: Diethyldibenzyldiamidotriphenylcarbinoltrisulphurous acid." He then noticed the members of the Academy recently deceased, such as Sir R. Owen and Prof. De Candolle. He quoted the reply of Dr. Charcot to the Bestiarians, who, with an ill-placed sensitiveness, oppose experimental physiology under the pretext of protecting animals. A tribute of honour was also paid to Dr. Lister and M. Moissan. With reference to the Montyon prize for statistics, the question may be raised whether statistics can be fairly ranked as a science, but rather as a method applicable in various sciences. The Jecker prize in chemistry was adjudged to M. de Forcrand, professor at the Faculty of Sciences at Montpellier. A prize was also adjudged to H. Gautier, for his researches on the action of chlorine on a group of compounds of the aromatic series, on the condition of iodine in solution, on its affinities when in solution, on the direct combinations of chlorine and bromine with metals, &c. The La Caze prize in chemistry was awarded to G. Lemoine. His researches relate to the phosphorus sulphides and their derivatives, to the allotropic transformation of phosphorus, and to the chemical equilibria between hydrogen and the vapour of iodine. It is announced that the Jecker prize (chemistry) will be awarded annually, and will be raised to the amount of 10,000 francs.

Bulletin de la Société Chimique de Paris. Series 3, Vols. ix. and x., Nos. 22.

Constitution of the Magentas.—A. Rosenstiehl.—A point well established is that rosaniline is an alcohol. In consequence it must be able to produce ethers by the action of acids. It is at the same time an amine, and forms salts. As it combines in its molecule these two functions, it must form with the acids two series of combinations. One of these series contains the characteristic grouping of the ethers, the other that of salts. In

rosaniline the ether function is satisfied by a mol. of hydracid. The amine function requires 3 mols. of hydracid. Experiment proves that rosaniline reacts in the first place with a single mol. of acid. The alcoholic function is satisfied in the first place, and the compound formed is an ether. When the first mol. of hydracid has completed its action, the amine function comes into play and fixes 3 mols. of acid.

Anilide of Gallic Acid, its Ethers, and its Salts.—P. Cazeneuve.—Already inserted.

On Bismuth Gallanilide.—P. Cazeneuve.—The bismuth gallanilide, the bismuth-methyl gallate, and the bismuth pyrogallol are analogous compounds which confirm the formula of bismuth gallate adopted by Causse.

No. 23.

Certain New or Very Rare Mineral Phosphates, and on The Genesis of Natural Phosphates.—Armand Gautier.—The author distinguishes the following aluminium phosphates:—Berlinite, Variscite, Callainite, Zepharowischite or Gibbsite, Wavellite, Fischerite, Peganite, Evansite, Turquoise. He proposes, however, to distinguish the aluminium phosphate of the Minerva cavern under the name Minervite. He considers that bibasic calcium phosphate and a part of the tribasic calcium phosphates found not only in the Minerva phosphorites, but in the rock guanos and other phosphates of animal origin, result from the direct action of ammonium phosphate of bacterian origin. But brushite, much more soluble than tribasic phosphate in waters charged with carbonic acid, is often carried away by them, whilst tribasic phosphate remains at its original place. The natural aluminium, iron, copper, &c., phosphates are formed by a similar process. Phosphatisation is attended by nitrification.

Nomenclature of the Ureic Compounds.—L. Maquenne.—A catalogue of these compounds with their old and new names, and with their formulæ.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxiii., No. 3.

Determination of Mercury in Dilute Solutions of Sublimate.—Prof. L. L. de Koninck.—In solutions of $\frac{1}{5000}$, or more, the precipitation of mercury as a sulphide and its gravimetric determination present no special difficulties. It is not the same with solutions at $\frac{1}{10000}$. In this case L. de Vignon recommends the colorimetric method. He treats the solution under examination with sulphuretted hydrogen, and compares the brown tint obtained with those furnished, under identical conditions, with solutions of mercuric chloride of known concentration.

Determination of Silicon and Aluminium in Commercial Irons.—Prof. L. L. de Koninck.—The difficulty in the determination of silicon and especially of aluminium in commercial irons is the comparatively enormous proportion of iron which these substances contain, and in certain procedures the necessity of obtaining reagents absolutely free from silica and alumina. It is almost impossible to obtain pure potassa or soda (?), and the commercial ammonia sold as pure contains almost always a little silica derived from the vessels in which it has been preserved. Ammonium carbonate dissolved immediately before it is used does not present this difficulty. To determine silicon and aluminium very accurately I propose the following method, founded upon certain qualitative assays executed by Dr. Leroux, my assistant. The metal is dissolved in nitric acid or aqua regia, and the solution is precipitated either by ammonium carbonate or ammonia if the metal is free from manganese, or in the contrary case by ammonium acetate, after basification by means of carbonate. If we wish to use ammonia we ascertain the absence of silica by evaporating a sufficient quantity in a *platinum* capsule, or by distilling the reagent and causing the vapour to pass at once into the solution to be precipitated. The ferric precipitate is collected, washed, and ignited. It is placed in a platinum boat, and heated in a current of hydrochloric gas. The ferric oxide is transformed into chloride, and is volatilised in this state, whilst the silica and alumina remain in the boat. To determine the alumina the silica may be driven off by means of hydrofluoric acid or ammonium fluoride. If the cast metal contains titanium or aluminium, these substances will be found along with the silica and alumina.

MEETINGS FOR THE WEEK.

MONDAY, 8th.—Medical, 8.30.
—— Society of Chemical Industry, 8. Discussion on Report of Patent Law Committee.
TUESDAY, 9th.—Royal Institution, 3. "Air, Gaseous and Liquid," by Prof. Dewar, M.A., LL.D., F.R.S.
—— Medical and Chirurgical, 8.30.
—— Institute of Civil Engineers, 8.
—— Photographic, 8.
WEDNESDAY, 10th.—Geological, 8.
THURSDAY, 11th.—Institute of Electrical Engineers, 8.
—— Mathematical, 8.
FRIDAY, 12th.—Astronomical, 8.

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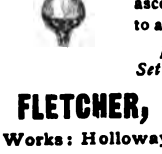

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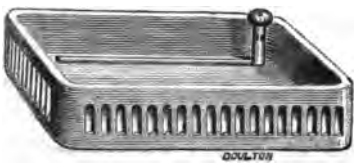

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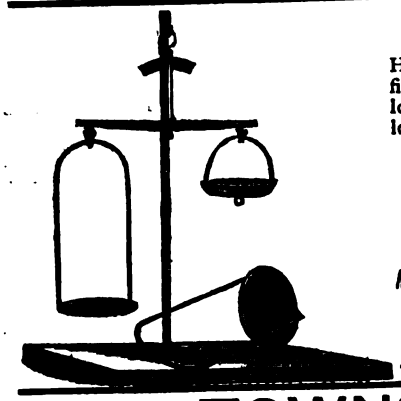

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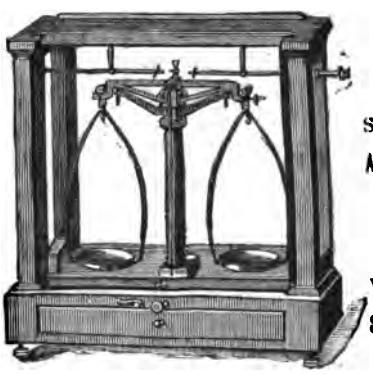

FIG. 3a.

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THE CHEMICAL NEWS.

Vol. LXIX., No. 1781.

THE DETERMINATION OF NICKEL.

By J. F. SLEEPER.

Since the discovery of the valuable properties imparted by nickel to steel gave a great impetus to the production of the first-mentioned metal, and consequently occasioned the appearance of it and its native and artificial combinations more frequently in the laboratory of the analyst, many methods have been proposed from time to time for its rapid yet accurate determination.

Some years ago, when engaged in much analytical work relating to the nickel manufacture, I became dissatisfied with the methods in ordinary use, and carried on a long series of experiments with the view of settling upon a fairly rapid and very accurate process, one that offered no inconvenience or uncertainty in manipulation, as is too often the case with those that depend upon evaporation of sulphuric solutions or preliminary precipitation as sulphide before plating. The result was the adoption of the process I am about to describe, and its use, with perfect satisfaction to the present day.

The substance to be analysed is :—

The nickeliferous material, of whatever variety, is now in solution, with a large excess of HCl present. The subsequent operations are nearly alike in all cases.

Pass H_2S rapidly through the *hot* solution for ten to fifteen minutes. Pt, As, Cu sulphides usually separate; the former is not infrequently present (especially in NiO) in small quantities. Filter, wash with H_2S water, and then boil off the H_2S. By this treatment the precipitation of fine sulphur is avoided when the solution is afterwards peroxidised with HNO_3, and an extra filtration dispensed with. Peroxidise by boiling (on wire gauze) with HNO_3. Boil five to ten minutes. Not a trace of H_2S must remain in the fluid, else NiS will contaminate the precipitate of NiH_2O_2 next obtained. Precipitate cautiously while boiling with sodium hydroxide solution.

This is prepared from C.P. caustic soda as free as possible from *carbonate* and *alumina* by placing a sufficient quantity of it in a beaker, pouring over it some *cold* water in small amount, and quickly agitating and draining off the fluid. Such treatment removes any superficial coating of carbonate which exposure to air may have encrusted the hydroxide with. Too great care cannot be taken to avoid its presence, as the well-known Na_2CO_3 (or $NaHCO_3$) forms in nickel solutions in presence of excess of alkali basic carbonate of nickel, which is not perfectly separated even by evaporation to dryness and treatment with boiling water, as zinc carbonate would be.

The residual soda is dissolved in boiling water and used for the precipitation of the NiH_2O_2, but little of it is lost if the washing has been adroitly performed.

Shot or Plate Nickel.

Break up the sample as much as possible, taking care to use a polished iron mortar of hard metal, to prevent contamination with iron, and directing only heavy vertical blows upon the material in the case of shot. Bore or cut off small pieces of plate. Mix well. Take 20 to 25 grms., transfer to a 2-litre flask, and dis. in 250 c.c. of dil. HNO_3 (1 pt. HNO_3 : 1 pt. H_2O) by aid of gentle heating; finally boil out fumes. Cool, dilute to the mark, agitate well. Draw out 50 c.c. with a pipette whose exact relation to the 2-litre flask used is known, so that a correction for any excess or deficiency of liquid held by it *when charged perfectly dry* can be applied. Discharge the contents into a porcelain caserole, and wash the liquid still adhering to the walls of the instrument *thoroughly* out with water. Evaporate to dryness with HCl. Take up with HCl and water, observing to make the acid constitute about $\frac{1}{8}$ to $\frac{1}{10}$ the volume of the fluid.

Matte or Ore.

Weigh out 1—5 grms., according to the presumed richness or poorness of the material. Dis. in aqua regia rich in nitric acid in a caserole, and evaporate with HCl and water to dryness. Dis. in HCl, dil. with H_2O, and add sufficient HCl to raise the amount of that acid to $\frac{1}{8}$ to $\frac{1}{10}$ the volume of the fluid.

Speiss.

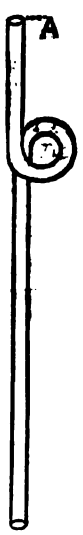
Take 1 grm., treat it with aqua regia in a caserole, and add "Br mixture" (saturated sol. of KBr in water shaken with excess of bromine) frequently. I have found this the most rapid and perfect mode of effecting solution. Evaporate with HCl, and take up with that acid and water, observing that the HCl amounts to $\frac{1}{8}$ to $\frac{1}{10}$ the bulk of the fluid.

Oxide.

Reduce the sample to the most impalpable powder possible in an agate mortar. Weigh out, from the sample dried one to one and a half hours at 130° C., 1 grm. into a carefully tared crucible of considerable capacity, and add about 10—15 grms. of $NaHSO_4$. By the use of $NaHSO_4$ a far more easily soluble melt is obtained than when $KHSO_4$ is taken, yet most chemists still employ the latter. Cover, except for a small space, with the lid, and raise the heat gradually to redness; as soon as foaming ceases urge it until the melt solidifies, cool somewhat, then introduce through the small space between the slightly raised lid and the rim of the crucible about 2 c.c. of the most concentrated H_2SO_4. If the right moment is taken advantage of during cooling in adding this, no spattering will occur. Cover, heat gently to fluidity, and cool. Wash out carefully with hot water into a caserole, and heat until sulphates are brought into perfect solution. If any residue remains, filter, wash twice, and subject the ignited ash to a second fusion with a *little* $NaHSO_4$; heat with a *small* quantity of H_2SO_4, wash out with hot H_2O, and add this to the main bulk. This second fusion is only necessitated when the oxide has not been properly ground, or the fusion not sufficiently protracted, with occasional agitation of the melted mass to wash down the sides of the crucible and dislodge particles withdrawn by foaming from the action of the flux. Add 7—10 c.c. of HCl. The total volume should be 75—100 c.c.

The precipitation is carefully effected under partial cover of a watch-glass in the boiling fluid (the fluid is apt to react violently on too rapid addition of the alkali). Stir constantly; as soon as the precipitate is permanent add a moderate excess of alkali, and boil fifteen minutes. Filter after standing ten to fifteen minutes on a water-bath to cause the subsidence of the flocks.

Filtration is best accomplished by the aid of a filter-pump—a carbon tube, bedded with glass and asbestos pulp, washed repeatedly with H_2SO_4 and then hot water as long as any trace of acid remains, or an ordinary 60° funnel with perforated platina cone and large paper filter being employed to retain the precipitate. If the pump is not at hand, choose a large filter of at least 6-in. diameter, cap it with a very small one to strengthen the apex, and fit it tightly into a suitable funnel. Attach to the stem of the funnel a "suction tube" (easily made by bending a glass tube 12—15 inches long and about $\frac{1}{8}$th inch internal diameter into the shape depicted in the cut) by means of a small piece of rubber tubing slipped on at A.



Bring on the clear fluid carefully, then the precipitate, wash once with boiling water; and then, with a suitable jet, rinse the precipitate from the filter, without *breaking* the paper, back into the same beaker, which has not been scrubbed out.

Heat the precipitate with 200—250 c.c. of boiling water, digest till settled on a water-bath, and bring upon the filter again, as before; still omitting to scrub out the beaker; wash well both beaker and filter with boiling water until the tested washings cease to precipitate acidified $AgNO_3$ solution.

Removal of all nitrates and chlorides is desired. The nickel has now been separated from these, and likewise from most of the Zn and Al present and the sodic salts. Have a *hot* mixture of 10 c.c. H_2SO_4 and 150—200 c.c. of water at hand. The H_2SO_4 should be measured, the water may vary within the limits specified—*all* the H_2SO_4 is to be used in this and subsequent operations.

Dissolve the $Ni(OH)_2+Fe_2(HO)_6$ on the filter by the aid of this mixture, wash well with cold water, collect the filtrate and washings in the beaker in which precipitation was effected, wash down the sides (to which some precipitate may adhere) with the same mixture, and dilute to 150—300 c.c. according to whether the iron is present in *small* or *large* quantity. To the *cold* fluid add an excess of concentrated NH_4HO, pouring it in *rapidly*. If the solution is *hot* and the NH_4HO added *slowly* the separation of the Ni from the Fe is much less perfect. I have always noticed this in sulphuric solutions. Stir briskly, let settle, decant the clear fluid above the precipitate upon a filter of suitable size (best using the pump, however), and wash once with water at ordinary temperatures. Merely rinse out the beaker well.

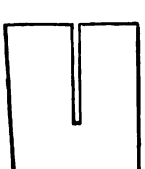
Dissolve the precipitate in some of the remaining H_2SO_4 mixture, receiving it in the same beaker. Wash down the sides of the latter with H_2SO_4 mixture, and dilute to 100—200 c.c. (according to the small or large per cent of Fe present). Precipitate with NH_4HO as before. Repeat this operation twice more in solutions of 50—200 c.c. bulk (controlled, as before, by the bulk of Fe noticed). Any H_2SO_4 mixture left over is added at the *finale*.

As fast as fresh filtrates are obtained, add them to the first, which has been previously set evaporating over a low Bunsen flame or a rose burner (or on a water-bath all night) at a temperature which is insufficient to cause it to dry up. Care should be taken that the heat is not allowed to rise so high as to cause the formation of hard rings of separated Ni salt around the sides of the dish; these would then require treatment with H_2SO_4 to remove them. When concentrated to 50—75 c.c. remove. (The concentrated saline solution should not be left for any great length of time in this state. I nearly lost an assay once by allowing it to stand over Sunday in the basin, the sulphates ascending in crusts nearly to the rim of the dish). Add NH_4HO to blue colour, then 5 c.c. excess. Filter into a beaker capable of holding with ease 200 c.c. Add 25 c.c. of concentrated NH_4HO. If any precipitate of $Fe_2(HO)_6$ or $Al_2(HO)_6$ appears on the filter it may contain NiH_2O_2, and *must* be re-dissolved in a mixture of H_2SO_4 1 part and water 2—3 parts, using as little as possible to avoid augmenting the H_2SO_4 content of the fluid to be electrolysed, and re-precipitated with NH_4HO. The filtrate thus obtained is then added to the larger one in the 200 c.c. beaker. Dilute to 200 c.c.

Platinum cylinders, measuring $2\frac{1}{2}$ inches high, and $2\frac{1}{4}$ inches in circumference, and of such stout foil as to weigh 20—21 grms. with gold soldered wire included, are used to receive the coating of Ni. Thinner foil would be contracted by the deposit of Ni, so as to even touch the inner pole if very thin. The inner pole is a cylinder of one-fourth the size of the outer, having a wire likewise soldered on with gold.

No gold should be exposed on the surface of the Pt anode; such I have known to dissolve off in the NH_4HO and plate down on the nickel, and also with it, blackening the latter, and left as black minute flocks on dissolving off the coating with dilute HNO_3. It was identified by tests. The platinum cylinder described should be cleaned by immersion in HNO_3, then in water, dipped in alcohol, dried at 100—110°, and weighed when cool.

Set up the electrodes (in a suitable holder with binding posts attached) and let them dip under the surface of the 200 c.c. of nickeliferous fluid until their bases are $\frac{1}{4}$ to $\frac{3}{16}$ inch from the bottom of the beaker, cover with a plate of mica having a longitudinal strip cut out as shown in the cut.



A current of 110 volts and 20 ampères, as furnished by the Edison Electric Company of New York, is employed. Two 24 candle-power incandescent lamps are introduced into the circuit in multiple arc, and the current turned on by a switch.

Plating rapidly ensues; in two or three hours all colour will have vanished from the electrolysed fluid. At intervals of one or two hours about 5 c.c. of concentrated

NH_4HO is added to the liquid to maintain a strong alkalinity, and occasionally the mica is rinsed to return any spirted up fluid to the main bulk.

I have never known any peroxide to separate and attach itself to the inner pole during the process, nor any Ni to scale off the outer.

To ensure good plating it is only requisite to comply with these conditions :—

1. Not to greatly exceed the total amount of H_2SO I specified—too much $(NH_4)_2SO_4$ causes dangerous foaming during plating.

2. To be sure NH_4HO is always in plentiful excess.

3. To suspend the electrodes in the electrolyte at a distance of not less than $\frac{1}{4}$ inch, nor more than $1\frac{1}{2}$ inch from the glass bottom. If less than the former, Ni *may* detach; if more than the latter, Ni may remain unplated in the undisturbed zone at rest below the electrodes.

4. To have separated Al and Fe so effectually that flakes of *consequence* do not separate during the plating, some Ni would be withdrawn by these from electrolysis.

5. To avoid the presence of even traces of nitrates.

The time taken for the plating varies with the amount of Ni present; on an average, about seven hours is requisite for 76 per cent Ni combined as NiO.

When the operation is complete remove the beaker quickly, turn off the current, wash the electrode rapidly with a jet of cold water, and dip the quickly disconnected outer cylinder into two beakers of water and two of alcohol successively, moving it up and down several times in each. Dry at 100—110° in an air-bath, cool, weigh. Increase in weight = metallic Ni (+Co, usually not estimated in technical work).

The filtrate is tested with colourless Na_2S and $\overline{A}$ for Ni; it should not give a yellow colouration, and the sulphur an adding $\overline{A}$ should be whitish.

The coating of nickel is beautifully bright and mirror-like on the surface towards the operator, shading at the margins into a dull frosted deposit. On the inner part it is dull silver-grey to light brownish, and granular. A very little impurity causes it to become smoky tinted and impairs its lustre. A firmly adherent deposit is always obtained.

The process from beginning to end is quite rapid when filter-pumps are accessible; it occupies about one day, but a much longer time is required when ordinary filtration is resorted to. No other method I have tried has yielded such a firm bright coat and well-agreeing results.

Pt, Cu, As are perfectly separated by the hot H_2S treatment they receive in a solution containing 1-8th to 1-10th its volume of acid, without carrying down NiS.

Test analyses show that differences range between 0·01 to 0·10 per cent, on duplicates and triplicates repeatedly run during some years, on 75 to 98 per cent Ni bearing material.

The electrodes after use may be quickly and perfectly cleaned by immersion in hot dilute HNO_3 (1 part to 6 of H_2O), in contact with the smaller ones used as anodes. The solution of $Ni(NO_3)_2$ thus obtained may be evaporated down if desired, and Co determined in it as usual.

Such are the details of this improvement in nickel determination. I have been careful to minutely describe all the various operations necessary, perhaps even to the verge of tediousness, that the process may not occasion trouble to those who give it a trial through any sins of omission committed by me.

Royal Institution.—On Tuesday next (January 16) Professor Charles Stewart will begin a course of five lectures on "Locomotion and Fixation in Plants and Animals." The Friday Evening Meetings will begin on January 19, when Professor Dewar will deliver a discourse on "Scientific Uses of Liquid Air."

NOTES ON THE OXIDES CONTAINED IN CERITE, SAMARSKITE, GADOLINITE, AND FERGUSONITE.*

By WOLCOTT GIBBS, M.D.,
Rumford Professor (Emeritus) in Harvard University.

(Continued from p. 11.)

Oxychlorides.—When the chlorides of the metals belonging to the cerium and yttrium groups, or, more generally stated, of the metals yielding the rarer earths, are carefully heated, oxychlorides are formed in greater or less proportion mixed with undecomposed chlorides. We may distinguish these as acid and basic chlorides. Water dissolves out the former very readily and leaves nearly or quite colourless basic chlorides, which are, relatively at least, insoluble. I find that in this way the earths present are separated into two groups, and that by repeating the operation upon each group a second differentiation is effected in each case. The process appears to deserve attention, and to compare very favourably with separation by means of basic nitrates. The details of this method are as follows :—

The mixed oxides, in as pure a state as possible, are to be dissolved in a small excess of pure chlorhydric acid; the solution is then to be evaporated at first on a water-bath, and then on a sand-bath, until a thick syrup is obtained. This is to be transferred to a porcelain crucible, which is then to be heated gently in a muffle. The heat should not be allowed to exceed low redness. Much chlorhydric acid is given off during the heating, and a white mass remains which consists in part of a mixture of oxychlorides, and in part of unaltered chlorides. The mass is then to be treated with hot water in rather small portions at a time, the solution being poured off before each new addition. When the washing is nearly complete the solution becomes turbid. The white insoluble mass and supernatant liquid are then to be evaporated to dryness, or to a thick syrup, after the addition of enough chlorhydric acid to effect complete solution. The liquid poured off and containing the soluble chlorides is also to be evaporated to dryness, but without addition of chlorhydric acid. We have then two separate portions, of which one, A, contains the soluble or relatively acid chlorides, and the other, B, the neutralised oxychlorides. Each of these portions is to be treated in the muffle, as in the first case. In this manner two new basic chlorides, B_2 and B_3, and two new acid chlorides, A_2 and A_3, are obtained. The same processes are to be repeated as long as the material lasts. The atomic mass of the oxides taken must first be determined, and afterwards the atomic masses of the portions A_1, A_2, A_3, &c., and B_1, B_2, B_3, &c. This enables us to determine the rate of change in the atomic masses produced by the successive operations. Of course, it is only necessary to take a small portion of each product, A_1, B_1, &c., for the determination of the atomic mass. The whole process will perhaps be rendered more clear by means of a diagram, and in illustration I shall select the results of actual work in a particular case. The starting-point in this case was a mixture of oxides from Texas gadolinite having the atomic mass 107·5. The data are as follows :—

(41)	0·3577 grm. gave	0·1357 grm.	C_2O_3 = 37·94	per cent.
(42)	0·3246 ,,	0·1228 ,,	C_2O_3 = 37·81	,,
(43)	0·3999 ,,	0·1515 ,,	C_2O_3 = 37·86	,,
(44)	0·6113 ,,	0·2814 ,,	R_2O_3 = 46·04	,,
(45)	0·6670 ,,	0·3064 ,,	R_2O_3 = 45·94	,,
(46)	0·6303 ,,	0·2892 ,,	R_2O_3 = 45·88	,,

Atomic mass 107·5.

B_1 Left. Atomic mass 110·8.

(47)	0·6836 grm. gave	0·3289 grm.	R_2O_3 = 48·11	per cent.
(48)	0·2344 ,,	0·0904 ,,	C_2O_3 = 38·57	,,

* *American Chemical Journal*, xv., No. 7.

A_1 Right. Atomic mass 94·75.

(49) 1·2740 grms. gave 0·4976 grm. R_2O_3=39·65 per cent.
(50) 0·2998 grm. „ 0·1065 „ C_2O_3=35·51 „

B_2 Left. Atomic mass 117·4.

(51) 0·4327 grm. gave 0·2157 grm. R_2O_3=49·84 per cent.
(52) 0·2860 „ 0·1089 „ C_2O_3=38·07 „

A_2 Left. Atomic mass 98·35.

(53) 0·7897 grm. gave 0·3714 grm. R_2O_3=47·03 per cent.
(54) 0·3772 „ 0·1566 „ C_2O_3=41·52 „

B_3 Left. Atomic mass 122.

(55) 0·5910 grm. gave 0·2803 grm. R_2O_3=47·43 per cent.
(56) 0·2023 „ 0·0710 „ C_2O_3=35·09 „

A_3 Left. Atomic mass 102·8.

(57) 0·4472 grm. gave 0·2137 grm. R_2O_3=47·78 per cent.
(58) 0·3067 „ 0·1248 „ C_2O_3=40·70 „

A_1 Right. Atomic mass 94·75.

(59) 1·2740 grms. gave 0·4976 grm. R_2O_3=39·05 per cent.
(60) 0·2998 grm. „ 0·1065 „ C_2O_3=35·51 „

A_2 Right. Atomic mass 91·65.

(61) 1·0032 grms. gave 0·3948 grm. R_2O_3=39·37 per cent.
(62) 0·5057 grm. „ 0·1856 „ C_2O_3=36·77 „

B_2 Right. Atomic mass 98·6.

(63) 0·7353 grm. gave 0·3291 grm. R_2O_3=44·75 per cent.
(64) 0·3343 „ 0·1318 „ C_2O_3=39·43 „

A_3 Right. Atomic mass 89·5.

(65) 0·4864 grm. gave 0·2146 grm. R_2O_3=44·12 per cent.
(66) 0·2212 „ 0·0929 „ C_2O_3=42·00 „

B_3 Right. Atomic mass 92·35.

(67) 0·5183 grm. gave 0·2238 grm. R_2O_3=43·17 per cent.
(68) 0·2080 „ 0·0834 „ C_2O_3=40·07 „

(To be continued.)

THE POLARISCOPE IN RELATION TO CHEMICAL CONSTITUTION.*

By PERCY FRANKLAND, Ph.D., B.Sc. (Lond.), F.R.S., Professor of Chemistry in University College, Dundee, St. Andrews University.

(Continued from p. 3).

A CIRCUMSTANCE which at once attracted the attention of chemists was the fact that all the ordinary active substances are obtained as the result of vital processes, either vegetable or animal, whilst whenever a substance containing an asymmetric carbon atom, and which is therefore capable of exhibiting activity, is prepared artificially, it is invariably found to be inactive to polarised light. Thus, whilst the lactic acid found in muscular tissue is active and dextro-rotary, the lactic acid artificially prepared by chemical means in the laboratory is invariably inactive and without influence on the polarised beam. That the inactive form should be obtained by artificial means, or in other words that the same quantity of each of the oppositely active isomers should be produced, is indeed to be anticipated according to the theory of probabilities. For inasmuch as there is, as far as we know, no more reason for the one isomer to be formed than the other, it is obviously "level betting" whether any individual molecule of, say, lactic acid produced is dextro- or lævo-rotary. So that in the production of what is practically an infinite number of lactic acid molecules, there will be an equal number of dextro- and lævo-rotary molecules, or in other words, the mixture of these oppositely active molecules will be inactive.

Thus again in the artificial production of tartaric acid it is racemic acid which is formed, *i.e.*, a combination of equal parts of dextro- and lævo-tartaric acids.

If this theory be correct it is obvious that by suitable means it should be possible to separate the active constituents of such an inactive mixture. The methods by which such inactive mixtures could be made to yield up their active components were already discovered by Pasteur many years ago; nor have any new methods been devised since, in spite of the numerous investigators who have devoted their attention to this matter.

The most important of these methods for decomposing such inactive combinations is a very remarkable one, depending upon the circumstance *that if such a substance is attacked or fermented by micro-organisms, the latter almost invariably decompose one of the optical isomers by preference.*

I will illustrate this method by means of an example which I discovered some years ago. One of the simplest substances containing an asymmetric carbon atom is glyceric acid, which is obtained by the oxidation of glycerin:—

CH_2OH	(CH_2OH)
$\vert$	$\vert$
$CHOH$	$(C)(H)(OH)$
$\vert$	$\vert$
CH_2OH	$(COOH)$
Glycerin.	Glyceric acid.

When so prepared, however, this glyceric acid is invariably found to be wholly inactive towards polarised light.

Some years ago I found a micro-organism, a bacillus, which has the property of inducing a fermentative decomposition of glyceric acid, and on studying this fermentation attentively I found that only a part, roughly one-half, of the glyceric acid was destroyed by the bacillus and converted into other products, whilst the glyceric acid which remained undecomposed proved to be powerfully active, viz., dextro-rotary. Thus the bacillus turned loose upon the inactive combination of the dextro- and lævo-rotary glyceric acids had singled out the lævo-rotary isomer for its destructive energies, and had left the dextro-rotary isomer intact. Thus:—

Inactive Glyceric Acid.

(CH_2OH)	(CH_2OH)
$\vert$	$\vert$
$+(C)(H)(OH)$	$-(C)(H)(OH)$
$\vert$	$\vert$
$(COOH)$	$(COOH)$
Dextro-rotary glyceric acid, left intact by bacillus.	Lævo-rotary glyceric acid, destroyed by bacillus.

In the same way I have, with Mr. MacGregor, quite recently obtained the dextro-lactic acid by the fermentation of ordinary inactive lactic acid with a suitable bacillus which decomposes the lævo-lactic acid by preference, thus:—

Inactive Lactic Acid.

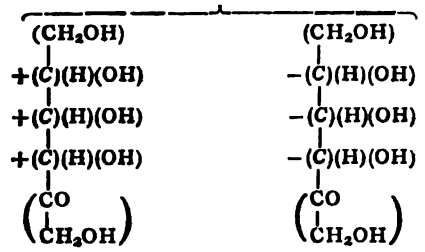
(CH_3)	(CH_3)
$\vert$	$\vert$
$+(C)(H)(OH)$	$-(C)(H)(OH)$
$\vert$	$\vert$
$(COOH)$	$(COOH)$
Dextro-rotary lactic acid, remaining after fermentation.	Lævo-rotary lactic acid. destroyed by fermentation with the bacillus.

Another exceedingly interesting example of this power of micro-organisms to select one of two optically isomeric substances was furnished a few years ago by Emil Fischer in his classical researches on the sugars. Fischer succeeded in building up by artificial means in the laboratory

* A Paper read before the North of England Institute of Technical Brewing, Manchester, Oct. 20th, 1893.

a sugar which was only distinguishable from the well-known lævulose by the circumstance of its being inactive to light, whilst lævulose, as you are aware, and as its name implies, turns the plane of polarisation powerfully to the left. To this inactive artificial sugar he gave the name of *Fructose*. On fermenting this with brewers' yeast, he found that only one-half of it was destroyed by the latter with formation of alcohol and carbonic anhydride, and that the residual half was now powerfully active to light, turning the plane of polarisation through exactly the same angle to the right that ordinary lævulose does to the left. The following formulæ will render this apparent:—

Inactive Fructose.



Ordinary lævulose (lævo-rotary) destroyed by fermentation with brewers' yeast.

Lævulose (dextro-rotary) not fermented by brewers' yeast.

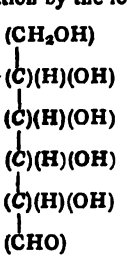
Thus the brewers' yeast selects for fermentation that form of lævulose which occurs in nature, and leaves that untouched which, as far as we know, is only an artificial laboratory product.

Having thus referred to these beautiful researches of Emil Fischer on the sugars, I should point out that they could have impossibly been carried on without the assistance of the theory of the asymmetric carbon atom, which has served as the guiding compass throughout Fischer's investigations.

The application of the asymmetric carbon atom to the series of sugar compounds is of so much theoretical interest to brewers that I will venture to say a few words more on the subject.

Nothing is better calculated indeed to demonstrate the value and importance of theory and of purely scientific investigation than the manner in which the theory of the asymmetric carbon atom has, in the hands of Emil Fischer, led not only to a complete elucidation of the relationship subsisting between the various sugars, but even to the successful artificial production in the laboratory of the three principal representatives of the sugar group, viz., *dextrose*, *lævulose*, and *galactose*, substances which are of such fundamental importance in the vital phenomena both of the animal and vegetable kingdoms, and which have been so extensively employed in some of the largest industries created by man.

Of the constitution of lævulose I have already spoken, and I will now refer only to the still more important dextrose, glucose, or grape-sugar, as it is variously denominated. The chemical constitution of this substance was proved by Kiliani, now about eight years ago, to be capable of representation by the following formula:—



Kiliani's formula for dextrose, glucose, or grape-sugar.

By applying our asymmetric carbon-atom theory to this formula we are able to predict a number of important points connected with this substance.

Thus it is at once apparent that four out of the six atoms of carbon which it contains are asymmetric, *i.e.*, each attached to four different groups. The four groups attached to each of these asymmetric carbon atoms can, as we have seen, be arranged in two different ways, to which we will give the sign + and − respectively, and on carefully examining the formula it will be seen that no less than sixteen different arrangements in all can be constructed, thus:—

1	2	3	4	11	12	13	14	15	16
+	+	−	−	+	+	+	+	+	−
+	−	+	−	+	+	+	−	−	+
+	−	+	−	+	−	−	+	−	−
+	+	−	−	−	+	−	−	−	−
				−	+	−	−	−	−
				+	−	−	+	−	−
				+	+	+	−	−	+
				+	+	+	+	+	−
				5	6	7	8	9	10

Our theory enables us, therefore, to predict the existence of no less than sixteen different modifications of grape-sugar. It enables us, moreover, to predict a number of other relationships subsisting between these isomeric modifications; thus of equal but opposite activity towards polarised light should be—

1, 4	5, 15	6, 16	7, 13
2, 3	11, 9	12, 10	8, 14

or in other words, there should be eight different types of glucose, each of which should exist in a left-handed and a right-handed modification respectively; whilst again by combining equal parts of 1 and 4, 5 and 15, 6 and 16, 7 and 13, 2 and 3, 11 and 9, 12 and 10, 8 and 14 respectively, we should obtain eight different types of glucose, each, however, inactive to polarised light.

Thus in all there should be twenty-four isomeric glucoses, sixteen active and eight inactive, the latter each composed of equal parts of equally, but oppositely, active isomers.

Although by chemical research only some of these substances have been hitherto obtained, yet there can be but little doubt that their preparation is only a matter of time, for in whatever direction the theory has been tested, it has not been found wanting.

Thus already now we are acquainted with no less than five different types of glucose, viz:—

Mannose	Dextro. Lævo. Inactive.
Glucose proper	Dextro. Lævo. Inactive.
Gulose	Dextro. Lævo. Inactive.
Galactose	Dextro. Lævo. Inactive.
Talose	—

or in all, therefore, thirteen out of the twenty-four isomers predicted.

(To be continued).

New Source of Rhodinol.—P. Monnet and P. Barbier.—The essential oil extracted from pelargoniums contains notable proportions of rhodinol, the characteristic constituent of the oil of roses.—*C. R.*, cxvii., No. 26.

ON THE

QUANTITATIVE SEPARATION OF METALS IN AN ALKALINE SOLUTION BY HYDROGEN PEROXIDE.

By P. JANNASCH and J. LESINSKY.

Separation of Lead from Zinc and Nickel.

1. *Separation of Lead and Zinc.*—For the separation of lead and zinc by the hydrogen peroxide method, about 0·5 grm. lead nitrate and 0·3 zinc oxide were dissolved in 50 c.c. water with the addition of 2 c.c. concentrated nitric acid, and there was then added in the cold a mixture of 40 c.c. hydrogen peroxide (2 to 3 per cent) and 15 c.c. concentrated ammonia, and, finally, 15 c.c. solution of ammonium carbonate. The mixture, which is of a reddish yellow colour, is now allowed to stand for some minutes with frequent stirring, filtered, and the precipitate is washed at first with dilute ammonia, and lastly with cold water. The dried lead precipitate is then treated exactly as it has been already directed for the separation of lead and copper.

The solution of zinc is evaporated down in a capsule of Berlin porcelain until the excess of ammonia is entirely expelled, 5 grms. of chemically pure sodium hydroxide are added, and the mixture is boiled until it no longer smells of ammonia; it is then acidulated with hydrochloric acid and the zinc precipitated as usual with sodium carbonate. The zinc oxide thus obtained is very easily contaminated with silica, and must be separately determined by solution in hydrochloric acid, evaporation to dryness, &c., and its weight must be deducted from the quantity just found. If the zinc oxide was absolutely pure it dissolves quickly and entirely in cold, dilute acetic acid. In this manner we may at the same time detect the possible presence of alumina.

It is certain that the separation of lead and zinc by hydrogen peroxide may also be effected under other conditions. We expect an exceptionally favourable result from the separation of the lead in a crystalline form, washing the precipitate with ammoniacal hydrogen peroxide in heat, &c.

2. *Separation of Lead and Nickel.*—For this separation there were dissolved 0·5 grm. lead nitrate and 0·4 grm. nickel-potassium sulphate in 50 c.c. of water, with the simultaneous addition of 5 c.c. concentrated nitric acid, adding 5 c.c. of acetic acid and 15 c.c. of strong ammonia in order to re-dissolve the lead sulphate formed. The lead is then precipitated as above with a mixture of hydrogen peroxide and ammonia. In the above case we used 75 c.c. hydrogen peroxide and 20 c.c. strong ammonia. A subsequent addition of ammonium carbonate is here not necessary, as the nickel oxide obtained on separation is always found perfectly free from lead. The precipitate of lead was flocculent (not crystalline) and was treated for weighing exactly as in the separation of lead and copper.

The ammoniacal nickel filtrate is evaporated to dryness, mixed with 15 c.c. concentrated hydrochloric acid (to expel acetic acid) and dried again. It is re-dissolved anew with the addition of a little dilute hydrochloric acid, and any silica separated is filtered off. This solution (about 250—300 c.c.) is heated to ebullition in a porcelain capsule, mixed with 4 grms. hydroxylamine chloride (in solution), and, finally, with stirring, with 60 to 70 c.c. of a 15 per cent pure soda-lye. The nickel precipitate does not appear at once, but only when the necessary quantity of soda-lye has been added, and not completely unless the liquid has boiled for a sufficient time (three to five minutes). We then dilute strongly with hot water, allow the precipitate to deposit, decant suitably several times, and then bring the precipitate upon the filter and wash carefully with boiling water.

In the above separations of lead the peculiar efficacy of large excesses of hydrogren peroxide have not yet been studied. The behaviour of lead precipitates in warmth and at the heat of ebullition has still to be studied. We are further engaged with the separations of bismuth from copper, cadmium, and other metals, and, in concert with J. Locke, the separation of iron and zirconium from cobalt, nickel, and titanium in ammoniacal solutions by means of hydrogen peroxide.—*Berichte der Deutsch. Chem. Gesell.*

THE BEHAVIOUR OF THE LIQUID ALLOY OF SODIUM AND POTASSIUM IN CONTACT WITH DRY OXYGEN GAS.

By G. STILLINGFLEET JOHNSON.

A short time ago I had almost completely exhausted a large desiccator in which was a dish containing the liquid alloy of sodium and potassium. It occurred to me that by introducing pure oxygen gas into the desiccator, and exhausting as completely as possible, any residual gas would be absorbed by the liquid alloy, leaving a vacuum more perfect than before.

The result of this experiment was entirely negative, *i.e.*, the mercury gauge showed absolutely no improvement in the vacuum, such as would have been produced by absorption of residual oxygen gas.

Subsequent experiments have shown that the liquid sodium and potassium alloy retains an untarnished lustre in *dry* oxygen gas at the ordinary temperature under pressures varying from slightly over the atmospheric pressure to a pressure of one-fiftieth of an inch mercurial column.

In one experiment I heated the alloy in dry oxygen. It kindled below a red heat, and burned with explosive violence, shattering the tube in which it had been contained. This is a somewhat interesting instance of the comparative inertness of dry gases.

King's College, London.

ON THE ESSENTIAL OIL OF LEMON.

By R. S. LADELL.

Many plants contain oily substances to which they owe their peculiar odour, and which can be obtained from them by distillation with steam. Many of the so-called essential oils contain terpenes or hydrocarbons represented by the formula $C_{10}H_{16}$; and it has been stated that the terpenes are often the chief constituents of the essential oils, as in the case of lemon and orange oils, &c. But it should not be forgotten that the oils of lemon and orange, as well as other essential oils, may be obtained entirely devoid of terpenes.

Geissler (*Pharmaceutische Centralhalle*, 1881) has described the terpeneless oil of lemon, and shown that it excels the commercial oil of lemon in odour, flavour, stability, solubility, and strength. The true terpeneless oil of lemon, which is the subject of this note, is an oxygenated liquid of constant boiling-point, specific gravity, and composition. Commercial oil of lemon has a specific gravity of 0·860 at 15° C.; the terpene known as citrene has a specific gravity of 0·850; whilst the *ordinary* terpeneless oil of lemon (*i.e.*, freed from citrene) has a specific gravity of 0·900. The ordinary terpeneless oil of lemon is really a mixture of several oxygenated compounds, but by fractional distillation a liquid has been obtained which has a constant composition, an exceedingly strong odour of lemon oil, a specific gravity of 0·962, a boiling-point of 206° C., and a specific rotatory power of $[\alpha]_D = + 6·42°$. The following results were obtained on submitting this liquid to analysis:—

0·5313 grm. gave 1·5135 grm. of CO_2 and 0·5617 grm. of H_2O.

	Found.	Calculated for $C_{10}H_{18}O$.
Carbon	77·6	77·92
Hydrogen	11·8	11·68
Oxygen	—	10·40

The above figures correspond with the empirical formula $C_{10}H_{18}O$ for the *true* oil of lemon—that is to say, for the terpeneless oil of lemon of constant composition. This oil appears to be an isomer of borneol. Further investigations are in progress, the results of which will be published in due course.

ON THE

CUPRIAMMONIUM DOUBLE SALTS.*

By THEODORE WILLIAM RICHARDS and HUBERT GROVER SHAW.

In the course of an extended investigation upon the ammoniacal compounds of copper, undertaken with the hope of obtaining more light upon the vexed question of their structure, a new class of interesting compounds was discovered. The preliminary notice of these compounds was published about a year ago;† but since that time several new ones have been added to the list. It is the object of this paper more fully to describe all of these substances, so far as they have been studied.

The generic feature of the new class is the fact that two different acids—a halogen and an organic acid radicle—are united at the same time to the ordinary cupriammonium group. Below are tabulated the formulæ of the compounds, the preparation, properties, and analyses of which are described in the work which follows:—

1. $Cu(NH_3)_2BrC_2H_3O_2$.
2. $Cu(NH_3)_3ClC_2H_3O_2 . H_2O$.
3. $[Cu(NH_3)_2ClC_2H_3O_2]_2 . 3NH_4C_2H_3O_2 + 7H_2O$.
4. $Cu(NH_3)_2BrCHO_2$.

Besides these compounds two others, which appeared as by-products of the investigation, are worthy of description:—

5. $CuCl_2 . 2NH_4C_2H_3O_2$.
6. $3\,CuBr_2 . 10NH_3$.

1. *Cupriammonium Acetobromide*, $Cu(NH_3)_2BrC_2H_3O_2$.

This compound is formed with great ease whenever cupric bromide is treated with alcohol and saturated ammonia water, and the mixture is nearly neutralised with strong acetic acid. For example, 5 grms. of cupric bromide were shaken with 10 c.c. of alcohol and the like volume of saturated ammonia water, until all of the copper was converted into cupriammonium bromide. The bright blue precipitate was then immediately dissolved in 60 or 70 c.c. additional of alcohol, and 16 c.c. of strong acetic acid. Upon cooling the solution, and allowing it slowly to evaporate in the air, large brilliant deep-blue crystals, which apparently belong to the monoclinic system, slowly separated (T. W. Richards, *Ber. d. Ch. Ges.*, 1890, p. 3791).

The same substance may be obtained in a similar manner from cupric acetate and ammonic bromide, after treating with ammonia and afterwards with acetic acid.

The new compound is only very slightly soluble in pure alcohol, and is decomposed at once by water into impure cupric hydroxide, ammonic acetate, and ammonic bromide. The cupric hydroxide contains large amounts of basic cupric bromide and acetate.

The only satisfactory solvent for it seems to be a strong aqueous solution of ammonic acetate and bromide, containing more or less alcohol. By this singular mixture the compound is not decomposed, even at 70° or 80° C. Acids of course at once decompose and dissolve cupriammonium acetobromide, and alkalis upon boiling set free ammonia and precipitate cupric oxide as usual. The crystals are fairly permanent in the air; they are singularly brittle and rather light, possessing a specific gravity of 2·134.

In the analysis of the compound, copper was determined electrolytically after evaporation with sulphuric and nitric acids; and the bromine and ammonia were determined as usual. The accurate determination of the acetic acid was a much harder task. Distillation with phosphoric acid, according to the method recommended by Fresenius (*Zeit. fur Analytische Chem.*, v., 315, and xiv., 172), is not very satisfactory because of the great expenditure of time which it requires, and the fact that traces of hydrobromic and phosphoric acids are always found in the distillate. Usually the two acids were precipitated together from the neutralised distillate, and the result was calculated as argentic bromide; but in some cases they were determined separately. The presence of phosphoric acid in the distillate is especially unfortunate, because of the uncertainty which it introduces in the end point of the alkalimetric reaction.

On the other hand, quantitative combustion after the usual method, and calculation of the acetic acid from the carbon dioxide formed, is not easy because of the presence of the large amount of bromine.

Analyses of $Cu(NH_3)_2BrC_2H_3O_2$.

I.—0·0685 gr. of the substance yielded 0·01865 gr. of copper upon electrolysis.

II.—0·1446 gr. of the substance distilled with caustic potash required 12·16 c.c. of a decinormal acid solution for neutralisation.

III.—0·08485 gr. of the substance yielded 0·06705 gr. of argentic bromide.

IV.—0·3173 gr. of the substance yielded 0·2518 gr. of argentic bromide.

V.—The distillate from a mixture of phosphoric acid and 0·2311 gr. of the substance required 10·11 c.c. of decinormal alkali for neutralisation. Approximately corrected for the alkalimetric equivalent of the argentic phosphate and bromide obtained from the distillate this amount becomes 9·90 c.c.

Many other analyses were made of subsequent preparations, in order to be sure of the identity of the crystals prepared in different ways. It is considered unnecessary to publish these, since they agreed essentially with those given above.

No.	Copper.	Ammonia.	Bromine.	$C_2H_3O_2$.
I.	27·23			
II.		14·35		
III.			33·63	
IV.			33·78	
V.				25·27
Average	27·23	14·35	33·70	25·27

Average Results.

	Calculated for $Cu(NH_3)_2BrC_2H_3O_2$.	Found.
Copper	26·87	27·23
Ammonia	14·42	14·35
Bromine..	33·79	33·70
Acetic acid	24·92	25·27
	100·00	100·35

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences.*

† Theodore W. Richards, *Berichte der Deutsch. Chem. Gesellsch.*, 1892, p. 1492. Since the publication of this paper, F. Foerster has announced the discovery of cupriammonium acetate (*Ber. d. Ch. Ges.*, 1892, xxv., 3416).

2. *Ammon-Cupriammonium Acetochloride,*
$Cu(NH_3)_3ClC_2H_3O_2 . H_2O$.

Almost any mixture which brings together in concentrated solution copper, chlorine, much acetic acid, and an excess of ammonia yields ammon-cupriammonium acetochloride upon the addition of alcohol. The substance consists of brilliant blue scales, having a pearly lustre. These crystals lose ammonia and water slowly upon exposure to the air, with marked alteration of colour; they are decomposed by water, a small amount of the copper going into solution. For analysis the crystals were pressed between filter-paper as rapidly as possible. A bromine compound similar in every respect to this one has been prepared, and will form the subject of a future communication.

Analyses of Ammon-cupriammonium Acetochloride.

I.—0·2524 gr. of the substance yielded on electrolysis 0·0698 gr. of copper.

II.—0·2273 gr. of the substance yielded 0·0634 gr. of copper.

III.—0·2875 gr. of the substance yielded 0·0808 gr. of copper.

IV.—0·1337 gr. of the substance required on distillation 17·37 c.c. of decinormal acid to neutralise the ammonia volatilised.

V.—0·1554 gr. of the substance required in the same way 20·17 c.c. of acid.

VI.—0·0979 gr. of the substance required 12·56 c.c. of decinormal acid.

VII.—0·2708 gr. of substance yielded 0·1704 gr. of argentic chloride.

VIII.—0·2696 gr. of substance yielded 0·1700 gr. of argentic chloride.

IX.—0·1926 gr. of the substance yielded upon distillation with phosphoric acid a distillate requiring 8·94 c.c. of decinormal baric hydroxide for neutralisation with phenolphthalein. This liquid yielded 0·0116 gr. of argentic chloride, containing traces of argentic phosphate, which amount is equivalent to about 0·81 c.c. of decinormal acid. Hence the acetic acid in the distillate must have required 8·13 c.c. of the alkaline solution.

X.—0·2215 gr. of substance required upon distillation 10·38 c.c. of baric hydrate, of which 0·66 were required to neutralise the hydrochloric acid corresponding to 0·0096 grm. of argentic chloride obtained from the neutralised distillate (10·38 − 0·66 = 9·72).

No.	Copper.	Ammonia.	Chlorine.	$C_2H_3O_2$.
I.	27·65			
II.	27·89			
III.	28·17			
IV.		22·16		
V.		22·14		
VI.		21·89		
VII.			15·56	
VIII.			15·59	
IX.				24·91
X.				25·90
Average	27·90	22·06	15·57	25·40

The averaged results are given below.

	Calculated for $Cu(NH_3)_3ClC_2H_3O_2 . H_2O$.	Found.
Copper	27·98	27·90
Ammonia	22·53	22·06
Chlorine	15·60	15·57
Acetic acid	25·97	25·40
Water (by difference)	7·92	9·07
	100·00	100·00

(To be continued).

ON THE

DECOMPOSITION OF LIQUIDS BY CONTACT WITH POWDERED SILICA, &c.*

By Dr. G. GORE, F.R.S.

It is recorded that dilute vinegar is to some extent deprived of its acid by filtration through pure quartz sand (Gmelin's "Handbook of Chemistry," i., 114). I have tested this statement by allowing pure very dilute acetic acid to filter at a rate of about two drops per minute through a narrow column, 9 inches high, of very fine white sand, which had been washed with distilled water, digested with hot and pure hydrochloric acid, washed again, ignited, digested with pure and strong acetic acid, washed again, and heated to redness. The first portions of liquid which passed through were quite neutral to litmus paper.

It is also stated that permanganate of potassium is removed from its aqueous solution by trickling through finely divided silica (J. J. Thomson, "Applications of Dynamics to Physics," p. 192). I repeated this experiment in a manner similar to the above, but the effect was extremely small, and complete precautions had to be taken to exclude all organic matter and dust, a mere trace of which would have been sufficient to produce the observed effect.

By similarly filtering a dilute solution of mixed sodium-potassium cyanide through the properly prepared pure sand, or by merely shaking the solution and sand together in a bottle and allowing the sand to settle, on analysing the clear liquid, in each instance, it was found to contain less cyanide than the original solution. I further found that pure precipitated silica, previously ignited, abstracted a very much larger proportion of cyanide from a solution of that salt by agitation with it in a bottle, than an equal weight of the finest sand.

In this research a number of liquids were examined, and those selected were in every case such as are usually considered not to chemically act upon or combine with the powder; and in every instance with silica the process of purifying the powder included digestion of it with the particular liquid which was to be absorbed, and repeated washing, &c., as above described. In certain cases the clear supernatant liquid, after filtration, was carefully tested for dissolved silica. In every instance chemical analyses were made of each strength of solution employed before and after the contact of the liquid with the powder, and in some cases these analyses were repeated. The quantities of substance stated were in all cases those of the anhydrous bodies.

In each of the following series of experiments the required amount of soluble substance was taken, and sufficient distilled water added to it to make it a total of 25 c.c. Fifty grains of the suitably prepared pure precipitated silica were then added, and the mixture well shaken in a stoppered glass bottle, then allowed to settle usually during sixteen to twenty hours, and the supernatant liquid filtered and analysed. In every instance the liquid expelled air from the silica. The substances employed (except chromic acid and potassium chlorate and cyanide) were of a high degree of purity, and in nearly all cases had been analytically examined beforehand. It was found by experience that the abstraction of the dissolved substance by agitation with the silica was completed in less than four hours. (See No. "117," also "Influence of Time.")

Experiments with Silica.

Solution. No.	Per cent.	Grains.	Per cent.
1.	0·25 HCl lost	0·008	= 0·89
2.	1·00 ,,	0·25	= 6·63

* From the *Proceedings of the Birmingham Philosophical Society*, Vol. ix., Part I.

Solution No.	Per cent.	Grains.	Per cent.
3.	5·00 HCl lost	0·35 =	1·82
4.	10·00 ,,	1·11 =	2·88

Each solution was volumetrically analysed with argentic nitrate.

No. 3 was repeated, and the same result was obtained. No silica was dissolved by the 10 per cent solution in sixteen hours.

5.	10·0 HBr lost	1·04 =	2·7

The acid was colourless, and was volumetrically analysed with Na_2CO_3.

6.	10·0 HI lost	0·387 =	1·0

Acid colourless and pure. Agitation with pure SiO_2 made it slightly red. Analysed as in No. 1.

7.	1·0 H_2SO_4 no effect		
8.	5·0 ,, lost	1·34 =	6·93
9.	10·0 ,, no effect		

Analysed as in No. 5. Repeated No. 8, and obtained similar results.

10.	10·0 CrO_3 no effect		

Volumetrically analysed with ferrous sulphate.

11.	1·0 HNO_3 no effect		
12.	5·0 ,, lost	0·35 =	1·83
13.	10·0 ,, ,,	0·96 =	2·50

Analysed as in No. 5. Repeated No. 11, and obtained similar results.

14.	10·0 $HClO_3$ lost	0·44 =	1·16

The acid contained a trace of HCl. Analysed as in No. 5.

15.	1·0 $HClO_4$ no effect		
16.	10·0 ,, lost	0·71 =	4·43

Acid colourless, contained a trace of $HClO_3$. Analysed as in No. 5.

17.	10·0 HIO_3 lost	0·89 =	2·3

Acid remained colourless after the trial. Analysed as in No. 5.

18.	1·0 H_3PO_4 no effect		
19.	10·0 ,, lost	0·63 =	6·65

Analysed as in No. 5.

20.	1·0 $H_4P_2O_7$ gain	0·05 =	1·32
21.	10·0 ,, lost	2·63 =	6·8

Analysed as in No. 5.

22.	5·0 oxalic acid no effect		

Analysed as in No. 5.

23.	10·0 tartaric acid lost	0·55 =	1·42

Analysed as in No. 5.

24.	10·0 citric acid no effect.		

Analysed as in No. 5.

25.	5·0 succinic acid lost	0·53 =	2·75

Analysed as in No. 5.

26.	1·0 $CuCl_2$ gain	0·123 =	3·19
27.	10·0 ,, ,,	0·86 =	2·24

Analysed as in No. 1.

28.	10·0 $CuSO_4$ lost	0·72 =	1·88

The amount of copper was found by precipitation as oxide.

29.	10·0 $NiCl_2$ no effect		

Analysed as in No. 1.

30.	10·0 $NiSO_4$ no effect		

The amount of salt was found by evaporation to dryness to a constant weight.

31.	10·0 $CoCl_2$ lost	0·92 =	2·4

Analysed as in No. 1.

32.	10·0 $CoSO_4$ gained	0·21 =	0·56

The two solutions were analysed as in No. 30.

33.	10·0 $FeCl_2$ no effect		

Analysed as in No. 1.

Solution No.	Per cent.	Grains.	Per cent.
34.	10·0 $FeSO_4$ lost	1·23 =	3·2

Analysed volumetrically with $KMnO_4$.

35.	10·0 $MnCl_2$ gained	0·42 =	1·1

Analysed as in No. 1.

36.	10·0 $MnSO_4$ gained	0·39 =	1·03

Precipitated and weighed as MnO.

37.	1·0 $CdCl_2$ lost	0·069 =	1·8
38.	5·0 ,, no effect		
39.	10·0 ,, lost	0·42 =	1·1

Analysed as in No. 1.

40.	10·0 $CdSO_4$ gained	0·51 =	1·3

Analysed as in No. 30.

41.	1·0 $ZnCl_2$ lost	0·25 =	6·52
42.	5·0 ,, ,,	1·45 =	7·50
43.	10·0 ,, ,,	0·89 =	2·32

Analysed as in No. 1.

44.	1·0 $ZnSO_4$ no effect		
45.	10·0 ,, gained	1·21 =	3·15

Precipitated as $BaCl_2$ and weighed as barium sulphate. The zinc was precipitated as carbonate, ignited, and weighed.

46.	1·0 $MgCl_2$ lost	0·081 =	2·1
47.	5·0 ,, ,,	1·33 =	6·9
48.	10·0 ,, ,,	1·00 =	2·6

Analysed as in No. 1.

49.	10·0 $MgSO_4$ gained	0·91 =	2·35

The amounts of salt were found as in No. 30.

50.	1·0 $CaCl_2$ lost	0·158 =	4·1
51.	5·0 ,, ,,	0·42 =	2·17
52.	10·0 ,, ,,	1·19 =	3·1

Analysed as in No. 1.

53.	1·0 $SrCl_2$ lost	0·13 =	3·4
54.	5·0 ,, no effect		
55.	10·0 ,, lost	0·85 =	2·2

Analysed as in No. 1.

56.	10·0 $BaCl_2$ lost	0·42 =	1·09

Analysed as in No. 1.

57.	1·0 LCl no effect		
58.	5·0 ,, ,,		
59.	10·0 ,, lost	0·51 =	1·33

Analysed as in No. 1.

60.	0·1 NaCl no effect		
61.	0·25 ,, lost	0·052 =	5·45
62.	1·0 ,, ,,	0·077 =	2·0
63.	5·0 ,, no effect		
64.	10·0 ,, lost	1·07 =	2·77

Analysed as in No. 1.

The 10·0 per cent liquid contained no dissolved silica after the trial.

65.	1·0 NaBr no effect		
66.	5·0 ,, lost	0·33 =	1·7
67.	10·0 ,, ,,	0·46 =	1·2

Analysed as in No. 1.

68.	1·0 NaI no effect		
69.	5·0 ,, ,,		
70.	10·0 ,, lost	0·81 =	2·1

Analysed as in No. 1.

71.	10·0 Na_2SO_4 gained	0·42 =	1·09

Estimated as in No. 44.

72.	5·0 Na_2HPO_4 lost	0·44 =	2·3

Analysed gravimetrically by means of $MgSO_4$.

73.	3·0 $Na_2B_4O_7$ no effect		

Examined as in No. 30.

Solution. No.	Per cent.	Grains.	Per cent.
74.	0·1 $NaHCO_3$ lost	0·03	= 7·8
75.	0·25 ,, ,,	0·042	= 4·34
76.	1·0 ,, ,,	0·101	= 2·63
77.	5·0 ,, ,,	0·54	= 2·83
78.	10·0 ,, ,,	0·89	= 2·30

Analysed volumetrically by means of H_2SO_4.
No silica was dissolved by the 10·0 per cent solution.

79.	0·025 Na_2CO_3 lost	0·08	= 83·4
80.	0·1 ,, ,,	0·144	= 37·6
81.	1·0 ,, ,,	0·77	= 20·0
82.	10·0 ,, ,,	1·16	= 3·0

No. 79 was tested approximately by means of test paper and comparison solution.
Nos. 80 to 82 were analysed as in No. 76.
No silica was dissolved by the 10 per cent solution.

83.	0·025 NaCy lost	0·083	= 86·7
84.	0·1 ,, ,,	0·064	= 16·6
85.	1·0 ,, ,,	0·59	= 15·4
86.	10·0 ,, ,,	1·27	= 3·3

No. 83 was examined as in No. 79. The solutions were made by adding Na to aqueous HCy.
Nos. 84 to 86 were analysed as in No. 1.
No silica was dissolved by the 10·0 per cent solution.

87.	0·1 KCl lost	0·0077	= 2·0
88.	0·25 ,, no effect		
89.	1·0 ,, lost	0·14	= 3·65
90.	5·0 ,, ,,	0·178	= 0·92
91.	10·0 ,, no effect		

Analysed as in No. 1.

92.	1·0 KBr lost	0·166	= 4·3
93.	5·0 ,, ,,	0·95	= 4·93
94.	10·0 ,, ,,	0·72	= 1·87

Analysed as in No. 1.
No silica was dissolved by the 10·0 per cent solution.

95.	1·0 KI no effect		
96.	5·0 ,, lost	0·77	= 4·0
97.	10·0 ,, ,,	0·46	= 1·2

Analysed as in No. 1.
No silica was dissolved by the 10·0 per cent solution.

98.	5·0 KIO_3 gained	1·22	= 6·34

Analysed by means of sodic hyposulphite.

99.	5·0 $KClO_3$ gained	0·079	= 0·41

Analysed by means of $FeSO_4$ and $KMnO_4$.

100.	5·0 KNO_3 no effect		
101.	10·0 ,, lost	1·47	= 3·82

Analysed by weighing as dry sulphate. No silica was dissolved.

102.	1·0 $KHSO_4$ lost	0·338	= 8·75
103.	5·0 ,, ,,	0·89	= 4·6
104.	10·0 ,, no effect		

Analysed as in No. 5.
No silica was dissolved during six days by the 10·0 per cent solution.

105.	10·0 K_2SO_4 gained	0·32	= 0·84

Analysed as in No. 44.

106.	1·0 $KHCO_3$ lost	0·39	= 10·2
107.	10·0 ,, ,,	0·44	= 1·16

Analysed as in No. 76.

108.	0·025 K_2CO_3 lost	0·08	= 83·4
109.	0·10 ,, ,,	0·139	= 36·1
110.	0·25 ,, ,,	0·396	= 34·0
111.	1·0 ,, ,,	1·02	= 26·6
112.	5·0 ,, ,,	2·51	= 13·0
113.	10·0 ,, ,,	3·12	= 8·05

No. 108 was examined as in No. 79.
Nos. 109 to 113 were analysed as in No. 76.
No silica was dissolved by the 5·0 or 10·0 per cent solutions.

Solution. No.	Per cent.	Grains.	Per cent.
114.	0·025 KCy lost	0·084	= 87·5
115.	0·25 ,, ,,	0·47	= 49·0
116.	1·0 ,, ,,	1·00	= 26·0
117.	5·0 ,, ,,	1·88	= 9·75
118.	10·0 ,, ,,	0·99	= 2·56

No. 114 was tested as in No. 79.
Nos. 115 to 118 were analysed as in No. 85. Silica digested only four hours. No difference was found either in Nos. 117 or in 118 after digestion during sixteen more hours.

119.	10·0 RbCl lost	0·93	= 2·4

Analysed as in No. 1.

120.	10·0 RbBr no effect		

Analysed as in No. 1.

121.	10·0 RbI lost	0·89	= 2·3

Analysed as in No. 1.

122.	10·0 Rb_2SO_4 lost	1·08	= 2·8

Analysed as in No. 30.

123.	1·0 AmCl lost	0·112	= 2·9
124.	5·0 ,, ,,	0·70	= 3·63
125.	10·0 ,, ,,	0·89	= 2·32

Analysed as in No. 1.

126.	1·0 AmBr no effect		
127.	5·0 ,, ,,		
128.	10·0 ,, lost	0·42	= 1·1

Analysed as in No. 1.

129.	10·0 Am_2SO_4 lost	0·39	= 1·01

Analysed as in No. 44.

130.	0·005 Am. sesquicarb. lost	0·0057	= 60·0
131.	0·025 ,, ,,	0·043	= 45·0
132.	0·1 ,, ,,	0·095	= 24·8
133.	1·0 ,, ,,	0·309	= 8·0
134.	10·0 ,, ,,	0·96	= 2·5

Nos. 130 and 131 were analysed by means of Nessler's colour test.
Nos. 132 to 134 were analysed as in No. 76.

135.	1·0 AmHO lost	0·8	= 20·9
136.	5·0 ,, ,,	1·47	= 7·6
137.	10·0 ,, ,,	2·62	= 6·8

Analysed as in No. 76.

138.	10·0 trimethylamine lost	1·05	= 2·72

Determined as in No. 76.

139.	0·002 Iodine lost	0·00295	= 38·0
140.	0·02 ,, ,,	0·0209	= 27·1

Found by colour test with H_2SO_3 and starch. The silica was digested during eighteen hours.

(To be continued).

Carborundum.—This substance has been represented as suitable for cutting and polishing the diamond. According to experiments detailed in *Science* this statement is incorrect. Carborundum is hard enough to cut sapphire and corundum, but it will not cut or polish diamond. Its surfaces can be scratched by diamond points. Its hardness is between 9 and 10.

Carboxylic Derivatives of Dimethylaniline.—Chas. Lauth.—The introduction of the carboxyl group into dimethylaniline in the ortho-position gives to the coloured derivatives chemical and tinctorial derivatives very different from those of the colouring-matters derived from dimethylaniline itself. The position occupied by this carboxyl group in the carboxylic dimethylanilines has a great influence on the reactions. When it is in ortho with respect to the amide group we obtain carboxylic colouring-matters; when it is in para we obtain non-carboxylic colouring-matters, identical with those of dimethylaniline; and when in meta the aptitude to form colouring-matters has almost entirely disappeared.—*Bull. de la Soc. Chim. de Paris*, ix.-x., No. 24.

CORRESPONDENCE.

IMPROVED UREOMETER.

To the Editor of the Chemical News.

Sir,—My attention has just been called to the fact that you published in your issue of November 3rd last (Chem. News, lxviii., p. 214) a description, with diagram, of an apparatus, under the above heading, which you attribute to Professor Hinds. Will you allow me to say that it appears to be an imperfect imitation of a pocket ureometer made for me by Messrs. Griffin, of Garrick Street, and improved by, and to be obtained of, Messrs. Squire, 413, Oxford Street.

The apparatus, of which the ureometer ascribed by you to Professor Hinds is a poor copy, has been in daily use by me for nearly twelve months, and has been seen and tested by a considerable number of medical men and analysts who have worked with me in consultation. It answers perfectly.—I am, &c.,

Mortimer Granville, M.D.

14, Hanover Square,
January 8, 1894.

TOXICOLOGICAL SIGNIFICATION OF COPPER.

To the Editor of the Chemical News.

Sir,—In connection with this subject (Chemical News, lxviii., p. 296) the following facts may be of interest:—

About the year 1873, while I was working as a machinist in a general repair shop, I noticed that whenever a piece of clean iron or steel came in contact with my perspiration it was at once covered with a bright coating of copper. So remarkable was it that it attracted the curious attention of a great many people. On account of the apparently inexhaustible supply of this copper, it was at first supposed to be absorbed from the brass and copper which I was daily handling; but none of the other persons working in the same room, and at the same work, exhibited this strange phenomenon. I left the machine shop shortly after that, and have not since then been engaged in any business that would bring me in contact to any great extent with copper in any form. Nevertheless this peculiar "copper mine" continued to yield about the same "out-put," and in the same manner, until 1881.

During the period from about 1867 to 1881 I had always been troubled with a small projecting process—of bone as I supposed—on the inner front edge of the right tibia. It was about the size of a small pea, and was very sensitive to the touch.

About June 1st, 1881, this supposed process became loose, swelled slightly, and turned as black as coal, imparting the same black colour to the surrounding flesh, but did not show any sign of festering, though it was very painful. About two weeks later it was cut out, and found to be a piece of corrugated sheet copper, about an eighth of an inch square and less than 1-100th of an inch thick. It was immediately recognised as a piece of a "waterproof" gun-cap, with which I remember distinctly having been wounded in the "shin" when a boy, some dozen or fourteen years previous, while "snapping caps." During at least eight years of that time this piece of copper had been continuously giving off and distributing through a human body enough copper to brightly copper-plate a piece of iron at any time by rubbing it on the back of the sweaty hand. Yet there was not at any time the slightest physiological inconvenience. In fact its presence would probably have remained unknown had it not been discovered in the manner described above.

It is worthy of note, also, as showing the minute divisibility of copper, that the fragment when taken out showed, from its size and thickness, that it could not have lost but a few m.grms. It was at least half as thick as the original gun-cap. It showed the corrugated surface on one side almost as perfectly as a new one. It was about an eighth of an inch square, and could not have been much larger than that originally.—I am, &c.,

Charles J. Reed.

Reed Electric Co., 625 and 627, Girard Avenue,
Philadelphia, Pa., Dec. 27, 1893.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxvii., No. 26, December 26, 1893.

Remarks on the Heating and the Spontaneous Ignition of Hay.—M. Berthelot.—The rise of temperature capable of causing the ignition of hay results from purely chemical reactions which bear upon products modified at first by fermentations.

Composition of Drainage Waters in Winter from Land Bare or Covered with Vegetation. — P. P. Dehérain. — The losses of nitric nitrogen from fallow lands are enormous. During the year—March, 1892, to March, 1893—four cases, without vegetation, have lost per acre 221·4 kilos., 193·1 kilos., 242·1 kilos., and 245·1 kilos. In land covered with vegetation the loss is reduced by a variety of causes.

Analysis of the Butters of Commerce.—C. Violette. —Already noticed.

Is there Oxygen in the Sun's Atmosphere? — M. Duner.—The author considers that the bands A, B, and α are of a purely terrestrial origin, and discusses the hypotheses proposed to account for the non-appearance of the spectral characters of oxygen which he considers as purely speculative.

Weight of a Litre of Normal Air, and on the Density of Gases.—A. Leduc. — The author proposes to refer the density of gases to nitrogen. The weight of a litre of normal nitrogen at Paris is 1·2570. Its mass at the pressure of one atmosphere, C.G.S., is 1·24006 grm.

Sketch of the System of Precise Atomic Weights founded upon the Diamond as a Standard. — G. Hinrichs.—The author condemns the use of hydrogen as a standard for atomic weights, and proposes instead carbon in the form of diamond. He holds that the standard material should be solid, compact so as to avoid absorptions, very hard to resist the mechanical effect of the necessary manipulations, and of great chemical resistance to permit of the elimination of alien impurities by, *e. g.*, ebullition in aqua regia.

General Method for the Volumetric Determination of Silver in any Form whatever. — G. Denigès. This paper will be inserted in full.

Stability in the Air of Solutions of Mercuric Chloride at 1-1000.—M. Tanret.—We may conclude from the author's experiments that, under ordinary conditions, air may be regarded as having no action upon a solution of sublimate in 1000 parts of distilled water, whilst it is decomposed by air charged with ammoniacal vapours.

Remarks on the Critical Pressures in the Homologous Series of Organic Chemistry.—E. Mathias.—By causing a substance to enter into several different homologous series, we calculate *a priori* its critical pressure.

On Caseine and its Organic Phosphorus. — A. Béchamp. — The author gives instructions for the detec-

tion and determination of phosphorus in caseine. He shows that caseine is the first instance of a definite chemical species containg six elements,—C_m, H_n, N_p, P_q, S_r, O_t.

On the Essence of Tarragon and its Conversion into Anethol.—E. Grimaux.—This memoir is not of sufficient importance to admit of insertion in full.

Presence of Camphene in the Oil of Spike.—G. Bouchardat.—The author's analyses show the complexity of the natural essential oils, which almost all contain turpentines boiling at 158°, citrenes which distil over at 178°, and, in certain cases, camphene which distils about 158°. All these carbides have the same composition, $C_{20}H_{16}$.

The Volatile Carbides of the Oil of Valerian.—M. Oliviero.—It seems to result from the author's experiments that the essence of wild valerian contains two carbides, $C_{20}H_{16}$, both boiling at 157—158°, a camphene slightly lævo-rotatory, and a lævo-rotatory turpentine, as well as some slightly lævo-rotatory citrene.

Contributions to the Study of the Ptomaines.—Oechsner de Coninck.—The author has submitted to limited oxidation the pyridic ptomaine, $C_{10}H_{15}N$. The acid compound obtained was found identical with the acid derivative of nicotine, $C_6H_5NO_2$.

Influence of Iron on the Vegetation of Barley.—P. Petit.—Ferrous salts are perfectly absorbed by barley, as is iron in organic combinations, and lead to a more intense assimilation of nitrogen. On the contrary, ferric sulphate acts as a true poison. This result throws some doubts on the general opinion of the pernicious action of ferrous salts, which are supposed to become harmless when peroxidised.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxiv., No. 2.

This issue contains no chemical matter.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. ix. and x., No. 24.

Reply to Signor Luzi on the Subject of Sprouting Graphite.—H. Moissan.—A question of priority.

On Isoconicine and Asymmetric Nitrogen.—L. Simon.—A reply to M. Ladenburg. The conception of Ladenburg joined to the negative experiments which he has made on tetrahydroquinoleine do not contradict each other, as he maintains. On the contrary, isomerism with a rotatory power of trivalent asymmetric can be manifested only in mols. already containing an atom of asymmetric carbon.

A New Electric Furnace. — Henri Moissan. — The author states that as the temperature rises lime, strontia, and magnesia crystallise in a few minutes. If the temperature reaches its maximum the very material of the furnace, quicklime, melts and flows like water. Carbon quickly reduces calcium oxide, and the metal is liberated abundantly. Chromic oxide and magnetic iron oxide melt rapidly at the outset of the experiment. Uranium sesquioxide heated alone is reduced to the state of black oxide. Uranium oxide, which is not reduced by carbon at the highest temperature of our furnaces, is rapidly reduced in the electric furnace. It is easy to obtain in ten minutes a regulus of 120 grms. of uranium. Nickel, cobalt, manganese, and chrome are reduced in a few moments.

Action of High Temperatures upon Magnetic Oxides.—Henri Moissan.—At temperatures ranging from 2000° to 3000° magnesia, lime, and strontia crystallise and then quickly melt. Boric acid, titanous oxide, and alumina volatilise rapidly; and the oxides of the iron group, stable at high temperatures, yield fused masses, bristling with small crystals. In all our experiments a mere rise of temperature determines the crystallisation of metallic oxides.

Analysis of the Ash of the Diamond. — Henri Moissan.—All the specimens of African bort and diamond examined contain iron. This metal forms the chief part of the ash. We have also found it in the ash of carbonado and diamonds from Brazil, except in a green kind of bort. We have detected in all the specimens the existence of silicon, and in most cases the presence of calcium.

Certain New Properties of the Diamond.—Henri Moissan. — The heat of combustion of the diamond varies in different specimens, ranging between 760° and 875°. In general the harder the diamond the higher is its combustion heat. If it resists at 1200° chlorine, hydrofluoric acid, and the action of certain salts, it is easily attacked, and this temperature by alkaline carbonates and this decomposition in a gaseous form enables us to establish that the specimen in question does not contain hydrogen or hydrocarbons.

Presence of Graphite, Carbonado, and of Microscopic Diamonds in the Blue Earth from the Cape.—Henri Moissan.—Our microscopic study of the "blue earth" has led us to discover the existence of numerous minute diamonds, of bort, of carbonado or black diamond, and lastly of graphite.

Study of the Meteorite of Cañon Diablo.—Henri Moissan.—The fragments of the meteorite examined contain transparent diamond, black diamond (carbonado), and a maroon-coloured carbon of low specific gravity.

On the Perfume of the Violet.—Ferd. Tiemann.—This bulky treatise does not admit of useful abstraction.

On the Acrylic Isomers of Berneol.—Ph. Barbier.—The conclusion of a series of articles not suitable for abstraction.

On some New Tropeines.—A. Petit and M. Polonovsky.—The authors have obtained and characterised phenylhomatropene and uretropine.

Determination of Ammonia in Gas Liquors.—E. Henry.—To prevent the indicator from being decolourised, the authors add to the alkaline solution a solution of lead sub-acetate.

MEETINGS FOR THE WEEK.

Monday, 15th.—Medical, 8.30.
Tuesday, 16th.—Royal Institution, 3. "Locomotion and Fixation in Plants and Animals," by Prof. Charles Stewart, Pres.L.S.
—— Institute of Civil Engineers. 8.
—— Pathological, 8.30.
Wednesday, 17th.—Society of Arts, 8. "White-Lead Substitutes," by A. Laurie, M.A.
—— Meteorological, 8. (Anniversary).
—— Microscopical, 8. (Anniversary).
Thursday, 18th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Chemical, 8. "The Molecular Formulæ of some Liquids as Determined by their Molecular Surface Energy," by Prof. Ramsay and Miss Emily Aston, B.Sc. "Contributions to Our Knowledge of the Aconite Alkaloids"—(VIII. On Picraconitine, by Prof. Dunstan, F.R.S., and E. F. Harrison; IX. The Action of Heat on Aconitine, by Prof. Dunstan, F.R.S., and F. H. Carr; X. Further Observations on the Conversion of Aconitine into Isaconitine, by Prof. Dunstan, F.R.S., and F. H. Carr). "The Interaction of Benzylamine and Ethyl Chloracetate," by Drs. Mason and Winder.
—— Royal Institution, 3. "The Life and Genius of Swift," by the Rev. Canon Ainger, LL.D.
—— Society of Arts, 8.30. "The Petroleum Fields of India—their Present Condition and their Probable Future," by R. D. Oldham, A.R.S.M.
Friday, 19th.—Royal Institution, 9. "Scientific Uses of Liquid Air," by Prof. Dewar, M.A., LL.D., F.R.S.
—— Quekett Club, 8.
Saturday, 20th.—Royal Institution, 3. "English Schools of Musical Composition," by Prof. W. H. Cummings.

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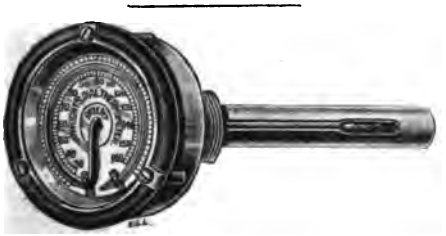

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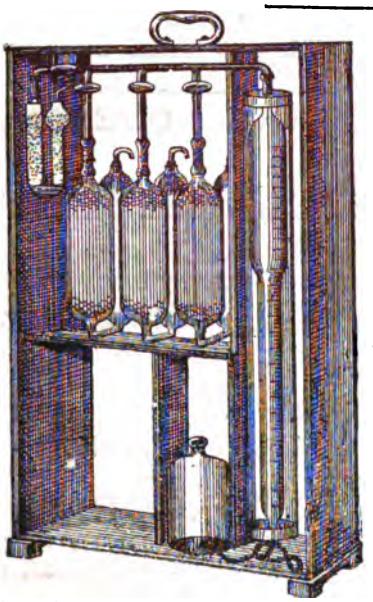

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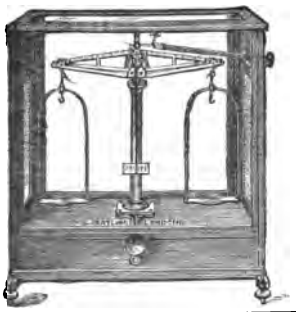

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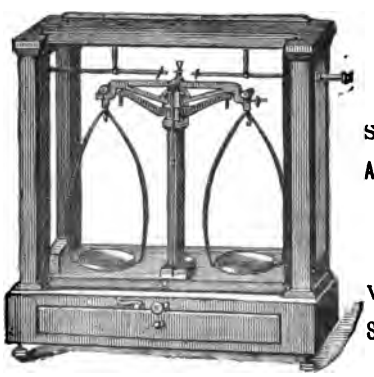

FIG. 3a.

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THE CHEMICAL NEWS.

VOL. LXIX., No. 1782.

NOTE ON THE TRUE ATOMIC WEIGHT OF CARBON.

By J. ALFRED WANKLYN.

THE drift of my work during the last few years appears to me to be that the real atomic weight of carbon is 6, and not 12 as is generally given at the present time.

The examination of one of the natural mixtures of hydrocarbons has furnished the following results, viz., by most persistent and methodical fractional distillation it has yielded the following series of liquids:—

	Boils at	Vapour Density. Found.	Theory.	
Aa ..	99° C.	3·69	3·63	$C_{7\frac{1}{2}}$ H_{15}
Ab ..		3·91	3·87	C_8 H_{16}
B ..		4·08	4·11	$C_{8\frac{1}{2}}$ H_{17}
Bb ..		4·36	4·35	C_9 H_{18}
Bc ..		4·59	4·59	$C_{9\frac{1}{2}}$ H_{19}
C ..		4·84	4·84	C_{10} H_{20}
D ..		5·02	5·08	$C_{10\frac{1}{2}}$ H_{21}
Dd ..		5·20	5·32	C_{11} H_{22}
De ..		5·51	5·56	$C_{11\frac{1}{2}}$ H_{23}
E ..		5·77	5·80	C_{12} H_{24}
F ..		6·08	6·04	$C_{12\frac{1}{2}}$ H_{25}
			6·28	C_{13} H_{26}
G ..	215°	6·53	6·52	$C_{13\frac{1}{2}}$ H_{27}
Gg ..	224°	6·83	6·77	C_{14} H_{28}

New Malden, Surrey.

THE ANALYSIS OF CHLORIDE OF ZINC.

By JOSEPH M. STOCKS, F.C.S.

IT is well known that chloride of zinc dissolves many metallic oxides, and for this reason it has long been used as a flux.

The commercial solution containing about 20 per cent of zinc, which is employed for its antiseptic and hygroscopic properties in sizing cotton, often contains oxide of zinc dissolved in the chloride of zinc. This oxide is objectionable, and, as the zinc present as chloride is the substance required, the oxide should be removed by adding water and then filtering before determining the amount of zinc present as chloride.

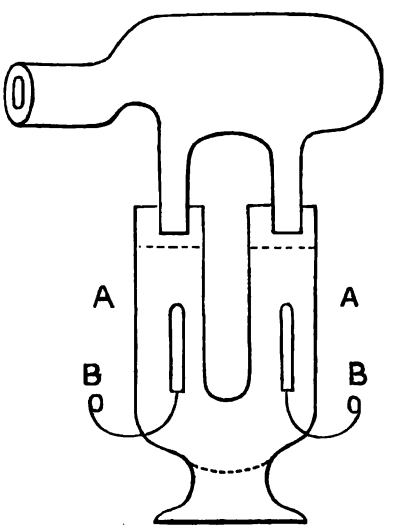
Neglect of this precaution by some analysts gives results which are too high; and when results obtained without its use are stated in terms of "chloride of zinc," considerable harm is likely to be done to analytical chemistry, because "they state the thing that is not."

The Tottington Science School,
January 6, 1894.

AN ELECTRIC BLOWPIPE.

By H. N. WARREN, Research Analyst.

THE difficulty of manipulating with hydrogen-gas in conjunction with oxygen when high temperatures are desired has for a long time past induced experimenters to substitute for the former coal-gas. This agent, although suitable for lime-light illumination, is far inferior as regards temperature to the use of pure hydrogen. During the past season the author has had occasion in several instances to test the efficiency of the two mixtures. Several refractory substances, melting readily by the aid of the pure oxy-hydrogen, were observed to obstinately refuse liquefaction at all when subjected to the influence of the latter compound; a blowpipe thus fed by a mixture of coal-gas and oxygen, even when both at the same pressure, is very weak as regards its action, the most serious drawback being the difficulty of obtaining a flame uniform; first the outer part of the flame being hottest, then the innermost. These difficulties will be found altogether obviated by using the electro-oxy-hydrogen blowpipe, as shown in the accompanying diagram, which after several different constructions as regards pattern, appears thus in one of its simplest and most effective forms: A A consisting of a



glass U-tube of suitable dimensions mounted upon stand and furnished with interior platinum plates; B B, in contact with acidulated water, which is introduced into the apparatus before using the same, the blowpipe in connection with the upper part allowing the gases to mix in the ordinary way. Thus is constructed the most effective blowpipe ever introduced to the scientific world; being perfectly automatic, of almost indefinite duration, and requiring no taps as regulators, the gases being evolved in exact proportion to re-form water, whilst the flame is regulated at will by means of the electric current. By similar construction upon a larger scale an automatic furnace may be arranged.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

ON THE CUPRIAMMONIUM DOUBLE SALTS.*

By THEODORE WILLIAM RICHARDS and HUBERT GROVER SHAW.

(Continued from p. 22.)

3. *Complex*† *Cupriammonium Acetochloride*, $[Cu(NH_3)_2ClC_2H_3O_2]_2 \cdot 3NH_4C_2H_3O_2 + 7H_2O$.

THE complex cupriammonium acetochloride is obtained under conditions which would have been expected to pro-

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*.

† "Complex" is used here in default of a word more capable of describing the complexity of the compound. It is not intended to carry with it any technical meaning with regard to the structure of the molecule. Indeed, the names of all the compounds described in this paper are far from satisfactory to us; they would be thrown out very gladly if better ones could be found.

duce the simple compound enclosed in the brackets above. This simple compound, probably owing to its great solubility, we have been unable as yet to isolate. Whenever cupric chloride is treated with a great excess of concentrated ammonia water, the excess cautiously neutralised with glacial acetic acid, and the whole treated with alcohol and allowed to evaporate, great crystals of the complicated compound containing three molecules of ammonic acetate and probably seven of water to every two of cupriammonium acetochloride always separate out. The addition of somewhat more acetic acid in this case constitutes the sole difference between the methods of preparing this compound and the preceding. In the former case an excess of ammonia was required.

The crystals of the complex salt are of a most brilliant blue with a tinge of violet, and may be obtained of almost any size. They dissolve in very small amounts of water without apparent decomposition, but larger amounts of water decompose them. The new compound readily loses water and ammonic acetate in the air, and is converted into a pale green powder, which remains to be investigated. Over caustic potash in a desiccator, on the contrary, it is soon converted into a pale violet powder with a very sudden loss of weight. After the sudden decrease has stopped a slower decrease continues, without change of colour, and the composition of the powder constantly approaches that of the simple cupriammonium acetochloride. Its complete conversion into this compound we have not yet been able to accomplish; and regarding the exact nature of the compounds which are marked by the irregular decrease in weight we have as yet nothing to say.

For analysis the crystals were pressed between filter-paper. The possible causes of error from decomposition on the one hand, and the adhesion of mother-liquor on the other, were guarded against as much as possible. Nevertheless these causes of error are undoubtedly responsible for the not unreasonable variations noticeable in the analytical results; for the three specimens of crystals analysed were undoubtedly identical.

Analyses of Complex Cupriammonium Acetochloride.

I.—0·2404 gr. of the substance yielded on electrolysis 0·0411 gr. of copper.
II.—0·2446 gr. of the substance yielded on electrolysis 0·0419 gr. of copper.
III.—0·2772 gr. of the substance yielded on electrolysis 0·0476 gr. of copper.
IV.—0·1418 gr. of the substance yielded on distillation enough ammonia to neutralise 13·25 c.c. of decinormal acid.
V.—0·1403 gr. of the substance required on distillation 13·24 c.c. of decinormal acid.
VI.—0·1895 gr. of the substance required on distillation 17·79 c.c. of decinormal acid.
VII.—0·1472 gr. of the substance required on distillation 14·19 c.c. of decinormal acid.
VIII.—0·2319 gr. of the substance yielded 0·0895 gr. of argentic chloride.
IX.—0·2244 gr. of the substance yielded 0·0870 gr. of argentic chloride.
X.—0·1679 gr. of the substance gave on combustion 0·0998 gr. of carbon dioxide.

No.	Copper.	Ammonia.	Chlorine.	$C_2H_3O_2$.
I.	17·10			
II.	17·13			
III.	17·17			
IV.		15·95		
V.		16·11		
VI.		16·03		
VII.		16·46		
VIII.			9·54	
IX.			9·59	
X.				39·95
Average	17·13	16·16	9·57	39·95

A fourth sample, which had a similar appearance, was found to contain 17·61 per cent of copper and 9·94 of chlorine. This had probably begun to lose water and ammonic acetate. A finely powdered specimen kept for eleven months over sodic hydrate was found to contain 25·8 per cent of copper and 14·35 of chlorine. Since the theoretical percentages corresponding to—

$$Cu(NH)_2ClC_2H_3O_2$$

are respectively 33·08 and 18·45, it is clear that the excess of ammonic acetate had not been wholly decomposed during the long exposure. Further experiments in this direction will be made in the near future.

Results.

	Calculated for $Cu_2(NH_2)_4Cl_2(C_2H_3O_2)_2(NH_4)_2.7H_2O$.	Found.
Copper	17·12	17·13
Chlorine	9·55	9·57
Ammonia	16·08	16·16
$C_2H_3O_2$	39·73	39·95

(To be continued).

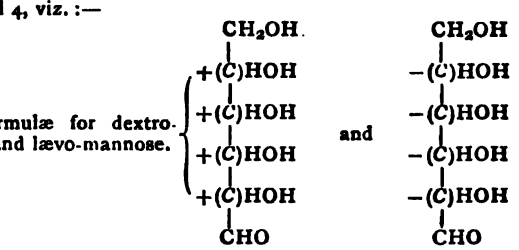
THE POLARISCOPE IN RELATION TO CHEMICAL CONSTITUTION.*

By PERCY FRANKLAND, Ph.D., B.Sc. (Lond.), F.R.S., Professor of Chemistry in University College, Dundee, St. Andrews University.

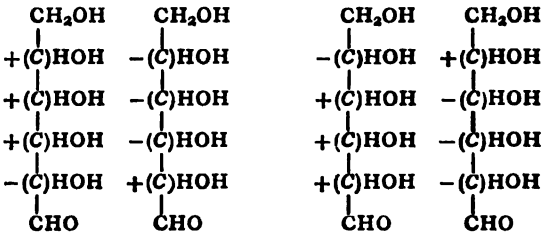
(Continued from p. 19).

But not only have these numerous isomers been already prepared, but in some cases it has actually been found possible to identify particular isomers with the formulæ in the above diagram. Thus, by a most admirable process of close reasoning, into the details of which I have not time to enter, Emil Fischer has shown that the two mannoses must have the arrangement indicated under 1 and 4, viz.:—

Formulæ for dextro- and lævo-mannose.



whilst in the case of the dextro- and lævo-glucoses proper he has similarly shown that we must select between the following two pairs of formulæ:—



Now it is here that the whole theory has been put to a most crucial test, and the brilliantly successful manner in which it has passed through this ordeal has enormously increased our confidence in its adequacy and usefulness.

* A Paper read before the North of England Institute of Technical Brewing, Manchester, Oct. 20th, 1893.

Thus the above formulæ indicate that there should be another sugar having exactly the same constitution as glucose, with the exception of the CH_2OH and COH groups being inverted. Now such a sugar has actually been artificially prepared by Fischer, for it is not known to exist in nature, and he has given to it the name of *gulose*, an appellation chosen in order to indicate its close relationship to glucose.

If it is not trespassing too much on your patience I will even briefly sketch the evidence upon which our knowledge of this remarkable relationship is based, thus:—

1. By gentle oxidation of a sugar of the glucose type the COH group can be converted into a COOH group. When subjected to this treatment glucose and gulose yield two distinct acids, gluconic and gulonic acids respectively, as should be the case assuming the correctness of the above formulæ:—

(CH_2OH)	(CH_2OH)
$+(C)(H)(OH)$	$-(C)(H)(OH)$
$+(C)(H)(OH)$	$+(C)(H)(OH)$
$+(C)(H)(OH)$	$+(C)(H)(OH)$
$-(C)(H)(OH)$	$+(C)(H)(OH)$
$(COOH)$	$(COOH)$

Formulæ showing the distinction between gluconic and gulonic acids.

2. By the further oxidation of such an acid it is possible to convert the CH_2OH group into a COOH group also, and by applying this treatment to gluconic and gulonic acids respectively it is found that the product obtained from each is the same, viz., saccharic acid, in precise accordance with what we should be led to anticipate from a consideration of our formulæ:—

$(COOH)$	$(COOH)$
$+(C)(H)(OH)$	$-(C)(H)(OH)$
$+(C)(H)(OH)$	$+(C)(H)(OH)$
$+(C)(H)(OH)$	$+(C)(H)(OH)$
$-(C)(H)(OH)$	$+(C)(H)(OH)$
$(COOH)$	$(COOH)$

Formulæ exhibiting the identity of the saccharic acid obtained from either glucose or gulose respectively.

In the following table I have collected the names of all the sugars at present known, and from this you will see how greatly the list has been swollen through these classical researches of Emil Fischer of which I have been endeavouring to give you some account.

Sugars of the Glucose Type.

Triose.

$C_3H_6O_3$ Glycerose.

Tetrose.

$C_4H_8O_4$ Erythrose.

Pentose.

$C_5H_{10}O_5$ { Arabinose.* / Xylose.* / Ribose.

Rhamnose.* $(CH_3C_5H_9O_5)$.

Hexose.

$C_6H_{12}O_6$ { Glucose, *d*,* *l*, *i*. / Mannose, *d*, *l*, *i*. / Fructose, *d*,* *l*, *i*. / Gulose, *d*, *l*, *i*. / Galactose, *d*,* *l*, *i*. / Sorbinose.* / B-Acrose.

Talose.

Rhamnohexose $(CH_3C_6H_{11}O_6)$.

Heptose.

$C_7H_{14}O_7$ { Mannoheptose. / Glucoheptose. / Galaheptose. / Fructoheptose.

Rhamnoheptose $(CH_3C_7H_{13}O_7)$.

Octose.

$C_8H_{16}O_8$ { Mannooctose. / Glucooctose.

Nonose.

$C_9H_{18}O_9$ Mannononose.

N.B.—In the above Table, *d* = dextrorotary, *l* = lævorotary, *i* = inactive. With the exception of those marked * all the above sugars have been discovered by Emil Fischer.

I think it must be admitted that it would be almost impossible to produce more convincing evidence of the enormous power which is conferred upon the investigator by the possession of a carefully framed theory, and when this theory touches some of the most invaluable substances which occur on our earth and leads to their artificial production by the hand of man, it should be possible also for the general public to realise, however faintly, the national duty of encouraging and fostering in every way possible the development of this mighty engine of pure scientific research.

(To be continued).

LIQUID ATMOSPHERIC AIR.*

By Professor DEWAR, M.A., LL.D., F.R.S.

THE prosecution of research at temperatures approaching the zero of absolute temperature is attended with difficulties and dangers of no ordinary kind. Having no recorded experience to guide us in conducting such investigations, the best instruments and methods of working have to be discovered. The necessity of devising some new kind of vessel for storing and manipulating exceedingly volatile fluids like liquid oxygen and liquid air, became apparent when the optical properties of the bodies came under examination. The liquids, being in active ebullition, were in a condition which rendered optical measurements impossible. All attempts at improvement on the principle of using a succession of surrounding glass vessels, the annular space between such vessels having the cool current of the vapour coming from the boiling liquid led through them, proved a failure. Apart altogether from the rapid ebullition interfering with experimental work, the fact that it took place involved a great additional cost in the conduct of experiments on the properties of matter under such exceptional conditions of temperature.

While suffering great anxiety on the question of expenditure, the Goldsmiths' Company came forward with the handsome contribution of £1000 to continue the work with improved apparatus. Personally, I desire to express my grateful thanks to the Goldsmiths' Company for tendering such encouragement and support.

* A Lecture delivered before the Royal Institution of Great Britain, Friday, January 20, 1893. (We are indebted to *The Engineer* for the loan of the woodcuts illustrating this article).

On careful consideration it became apparent that the proper way of attacking the problem was to conduct a series of experiments on the relative amounts of heat conveyed to boiling liquid gases; firstly, by means of the convective transference of heat by the gas particles, and, secondly, by radiation from surrounding bodies. The early experiments of Dulong and Petit on the laws of radiation had proved the very important part played by the gas particles surrounding a body in dissipating heat otherwise than by pure radiation. In the year 1873 I used a highly-exhausted vessel in calorimetric experiments "On the Physical Constants of Hydrogenium" (*Trans., Roy. Soc. Ed.*, vol. xxvii.) and the subsequent investigations of Crookes, and especially of Bottomley, having confirmed the great importance to be attached to the gas particles in the gain or loss of heat, it naturally occurred to me that the use of high vacua surrounding the vessels containing liquid gases would be advantageous. In order to arrive at definite data, some means of conducting comparative experiments between the amount of convective and radiant heat at such low temperatures had to be devised.

The apparatus shown in Fig. 1 measures the relative volumes of gas distilled in a given time under definite conditions, so that the measure of the gas distilled is proportional to the amount of heat conveyed to the liquid. The experiments are made in the following way:—The distilling vessel to the right consists of two concentric spherical chambers, the space between being highly exhausted by a mercurial air pump. The inner sphere is filled with liquid ethylene, oxygen, or air, and the whole apparatus immersed in water maintained at a constant temperature. Distillation begins immediately and continues at a constant rate provided the liquid in the bulb is maintained at the same level. This is not possible, but a sufficient uniformity is attained by making the observations during the evaporation of the first fourth of the contents. Having measured the volume of gas produced per minute when the sphere is surrounded with a high vacuum, the vessel is taken out of the water, the end nipped off, air allowed to enter, and then again closed. In this condition the inner sphere is filled up again with the liquid and the above experiment repeated. The following results were obtained, using ethylene and oxygen respectively:—

Liquid oxygen, vacuum	170 c.c. per minute.		
,, ,, air	840	,,	,,
,, ethylene, vacuum.. ..	56	,,	,,
,, ,, air	250	,,	,,

These results prove that under the same conditions a high vacuum diminishes the rate of evaporation to one-fifth part of what it is when the substance is surrounded with air at atmospheric pressure, or, in other words, liquid oxygen or ethylene lasts five times longer when surrounded with a vacuous space.

The next step was to construct a series of glass vessels surrounded by a vacuous space, suitable for various experiments, and such are represented in Fig. 2. In vessels of this kind, if the vacuum is very high, no ice appears on the surface of the outer vessel, even although the walls of the vacuous space are within half an inch of each other, and the liquid oxygen or air evaporates almost solely from the surface, no bubbles of gas being given off throughout the mass of the liquid. So far, the convective transference of heat has been stopped by the use of a high vacuum, but if the inner vessel is coated with a bright deposit of silver, then the radiation is diminished also, with the result that the rate of evaporation is further reduced to more than a half. In such vessels liquid oxygen or liquid air can be kept for hours, and the economy and ease of manipulation greatly improved.

The arrangements represented in Fig. 2 may be employed to study the law of radiation at low temperatures. All that is necessary for the purpose is to immerse the outer vessel in liquids maintained at different temperatures. The following preliminary results have been obtained, using oxygen, which boils at −180° C., in the inner sphere:—

Temperature.	Radiation.
−115° C.	60 c.c.
− 78° C.	120 ,,
+ 6° C.	300 ,,
+ 65° C.	600 ,,

These results show that radiation (along with such convective transference as remains) grows approximately at the rate of the cube of the absolute temperature. Many further experiments must, however, be made before the real law of radiation at low temperatures can be strictly defined.

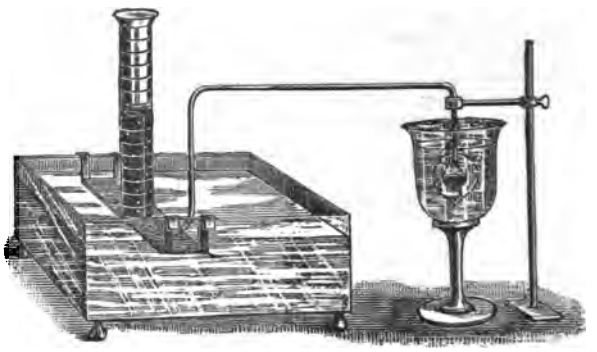


Fig. 1.

To produce exceedingly high vacua in vessels used for such purposes as the collection and storage of liquid air, a mercurial vacuum made in the following manner has been found highly satisfactory. Take, as an illustration, a glass vessel shaped like Fig. 3, and after placing in it a quantity of mercury, and connecting the pipe, H, with a good working air-pump, place in an oil- or air-bath heated above 200° C., and distil off a good quantity of the mercury. While the distillation is taking place the tube is sealed off at the point, A, and the bulb instantly removed

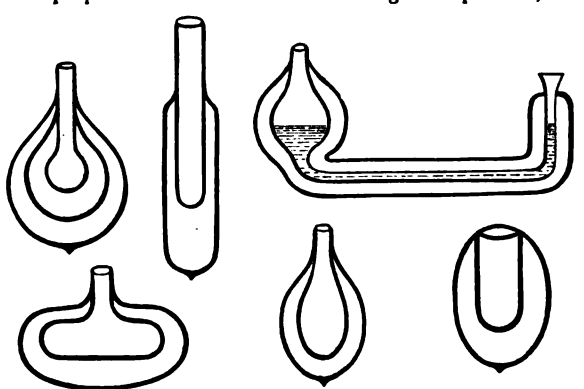


Fig. 2.

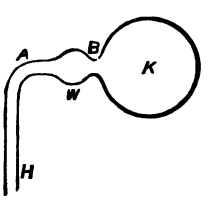


Fig. 3.

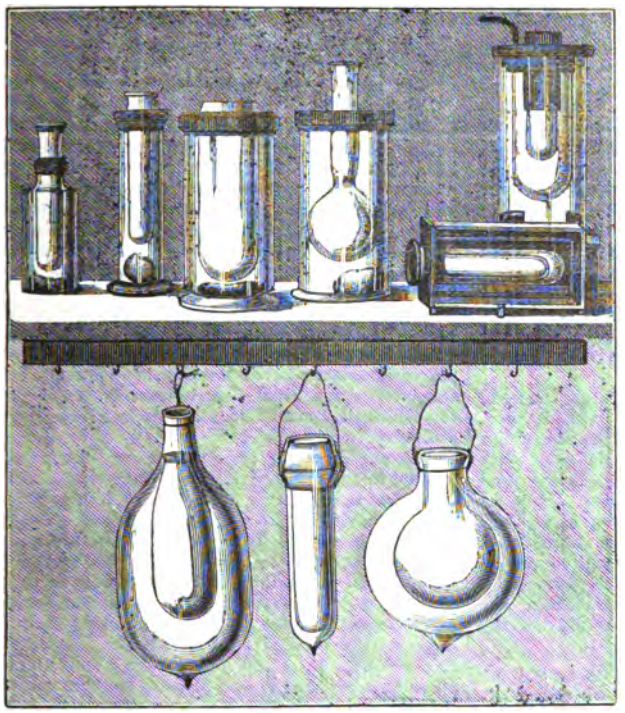


FIG. 4.

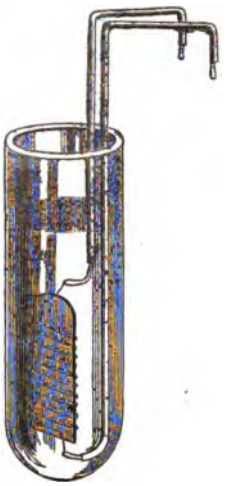


FIG. 5.

from the heated bath to such an extent as to allow condensation to take place in the small chamber marked B W in the figure. As the air-pump can maintain a vacuum of 10 m.m., no difficulty arises in sealing the glass tube during the continuance of the distillation. In some cases the mercury in the vessel has been heated up to near its boiling-point in air, and then the air-pump started, causing thereby an almost explosive burst of mercurial vapour which very effectually carries all the air out of the vessel.

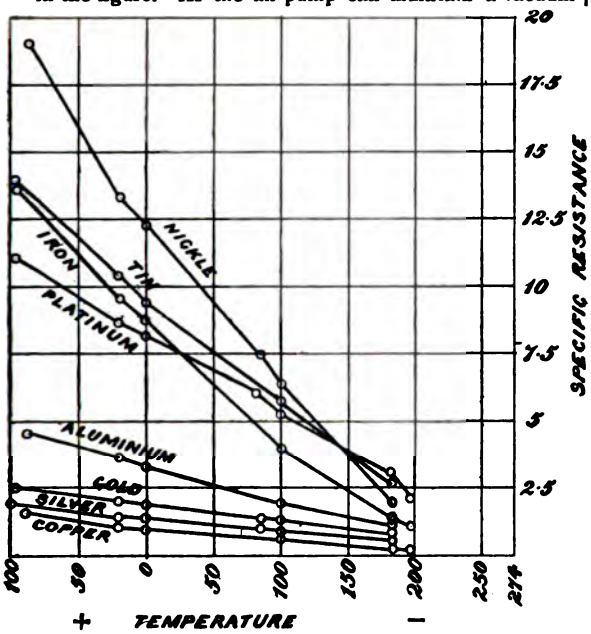


FIG. 6.—Electrical Resistance of Metals at Low Temperature.

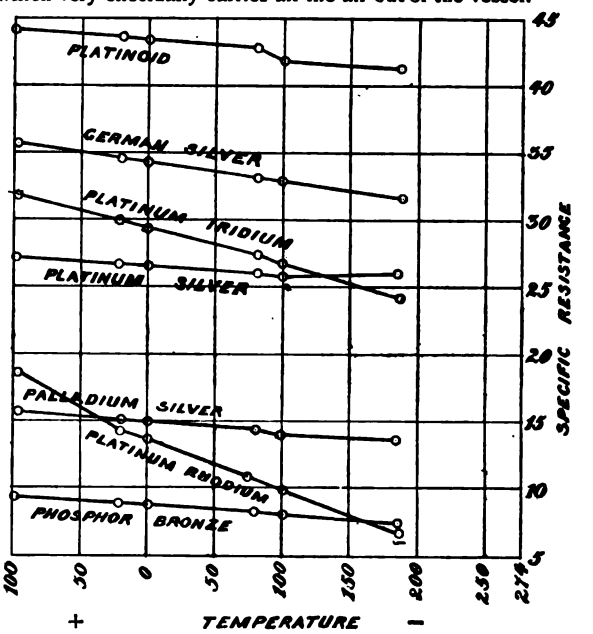


FIG. 7.—Electrical Resistance of Alloys at Low Temperatures.

After cooling, the vessel is removed from the bath, and the excess of mercury brought into the small bulb, B W, care having been taken to remove any small globules of

mercury, which adhere with great tenacity to the surface of the glass, by heating K while the part B W is kept cool. In this way the vessel K is filled with nothing but mercurial vapour, the pressure of which depends solely on the temperature of the liquid mercury contained in the small enlargement, and as this can, if necessary, be cooled to −190° C. by immersing it in liquid air, we have the means of creating in K a vacuum of inconceivable tenuity. It is sufficient for the production of very good vacua to cool the mercury in B W to −80° C. (using solid carbonic acid as the cooling agent), and while in this condition to seal off the bulb containing all the condensed mercury, so that K is left full of saturated vapour at −80° C. When very high exhaustions are required it is better not to seal off the mercury bulb, as the glass is apt to give off some kind of vapour. A similar mode of proceeding is adopted when other shaped vessels have to be highly exhausted, and no difficulty has arisen in operating with vessels having the capacity of more than a litre.

The perfection of the vacuum, assuming that nothing remains but molecules of mercury in the form of vapour, depends upon the temperature to which the subsidiary bulb is cooled. The well-known law which expresses approximately the relation between temperature and pressure, in the case of saturated vapours, must be assumed to be applicable to mercury vapour at temperatures where direct measurement becomes impossible. Having calculated the constants of a vapour-pressure formula from observed data at high temperatures, it is easy to arrive at a value of the vapour-pressure for any assumed lower temperature. Such a formula as the following,—

$$\text{Log. } P = 15{\cdot}1151 - 2{\cdot}2931, \text{ log. } T - \frac{3665{\cdot}7}{T},$$

where P is pressure in millimetres of mercury and T is the absolute temperature, agrees well with the experimental results. This formula gives the vapour-pressure at 0° C. as 0·00018 mill., and at −80° C. as 0·000,000,003 mill., or, respectively, about the sixth and the four hundred thousandth of a millionth of an atmosphere. Such a high vacuum could never be reached by the use of any form of mercurial air-pump. The electric discharge in such vacua produces intense phosphorescence of the glass, giving thereby a continuous spectrum, which makes the detection of the mercury lines difficult.

Consider for a moment the proofs that could be adduced that mercury vapour, even below a millionth of an atmosphere-pressure, can behave like an ordinary saturated vapour. The most characteristic property of a space filled with any saturated vapour is that cooling to a lower temperature causes partial condensation of the vapour in the form of liquid or solid. The amount of vapour in a mercurial vacuum at the ordinary temperature would weigh about the tenth of a m.grm. in the volume of a litre, and to see such an amount of the metal it would require to be concentrated on a small area in the form of a fine metallic film. Experiment has shown that the fifth of a m.grm. of gold may be made to cover one square c.m. of surface, so that a minute quantity of metal can be observed if properly deposited. This can be easily achieved in such mercurial vacua by cooling a small portion of the surface of the glass to the temperature of −180° C. by the application of a pad of cotton-wool saturated with liquid oxygen. In an instant the vapour of mercury deposits in the form of a brilliant mirror, which, on the temperature rising, becomes subdivided into a mass of exceedingly minute spheres of liquid. A repetition of the cooling does not bring down a new mirror, provided the first area is maintained cool; but if the vessel contains excess of liquid mercury any number of mirrors of mercury may be deposited in succession.

Mercury is thus proved to distil at the ordinary temperature when the vapour-pressure is under the millionth of an atmosphere. Further, it is easy to prove in this way that the cooling of the liquid mercury in such a subsidiary vessel (which has been described as a temporary part of the vacuum vessel) greatly improves the vacuum. For this purpose it is sufficient to cool the said vessel with some solid carbonic acid, and then to try and reproduce a mirror of mercury in the way previously described. No mercury mirror can be formed so long as the cold bath is maintained. If a piece of blotting-paper, cut into any desired shape, be moistened with water, and then applied to the surface of one of the vacuum vessels containing excess of liquid mercury, the local reduction of temperature produced by the evaporation soon causes a rough image of the paper to appear in the form of minute globules of condensed mercury. Such experiments support the view that the laws of saturated vapours are maintained at very low pressures.

In Fig. 4 specimens of the old and new vessels for collecting and manipulating liquid gases are shown. In each of the old forms it will be noted that a mass of phosphoric anhydride placed in the lower portion is required to absorb traces of water, otherwise the vessels are useless for optical observations. The vacuum receivers get over this difficulty.

The perfection of the vacuum in different vessels, all treated in the same way, differs very much, and after use they almost invariably deteriorate. The relative rates of evaporation of liquid oxygen under the same conditions in different vessels is the best test of the vacuum. In many of the large vessels used for the storage of liquid gases it is convenient and more effective to cause the deposition of a mercury mirror over the surface of the inner vessel (by leaving a little liquid mercury in the lower part of the double-shaped flask), instead of silvering as previously described. Under such conditions the mercury instantly distils and forms a brilliant mirror all over the surface of the inner vessel. The fact that mercury has a very high refractive index and is a bad conductor of heat are factors of importance in retarding the conveyance of heat. After the mercury mirror has been formed any further increase in the thickness of the film can be prevented, and at the same time the vacuum improved by freezing the excess of liquid mercury in the lower part of the vessel. The vacuum vessels described equally retard the loss as well as the gain of heat, and are admirably adapted for all kinds of calorimetric observations. The future use of these vessels in thermal observations will add greatly to the accuracy and ease of conducting investigations. The double spherical form of vacuum vessel is excellent for showing that the elevation or depression of a given volume of air a few feet causes an increase or diminution of volume, due to the small change of atmospheric pressure. The volume of air in the inner sphere is guarded from any sudden change of temperature by the surrounding highly vacuous space. This is only one of the many uses to which such receivers can be put.

In making vacua many other substances have been examined along with mercury, but they have not given equally satisfactory results.

Sulphur would occur to anyone as a substance that might replace mercury, seeing the density in the form of vapour, and also the latent heat of vaporisation, are nearly identical; and it has the further advantage of being a solid at ordinary temperatures. The sulphur vacua have, however, so far not been an improvement, chiefly because traces of organic matter are decomposed by the sulphur, giving sulphuretted hydrogen and sulphurous acid, gases which are dissolved by and remain in the sulphur.

When the surface of such a sulphur vacuum is cooled with liquid oxygen in the manner previously described, a faint crystalline deposit occurs, only it takes a much longer time to appear than in the case of the mercury vacuum. If a similar vessel is boiled out, using phosphorus as the volatile substance, the application of liquid oxygen to the surface causes instant deposition. Thus it can be proved sulphur and phosphorus distil at ordinary temperatures just like mercury.

An investigation as to the electric conductivity of metals, alloys, and carbon at low temperatures, has been undertaken in conjunction with my friend Professor J. A. Fleming, D.Sc., F.R.S. The experiments are made by means of a resistance-coil shown in Fig. 5, consisting of a piece of notched mica coiled with the fine wire to be tested, and of stout insulated copper-rod connections. The coil and connection are immersed in liquid oxygen contained in a vacuum test-tube, and the temperature of −200° C. can be reached by exhausting the oxygen by means of a powerful air-pump. The results point to the conclusion that absolutely pure metals seem to have no resistance near the zero of temperature as indicated by the above curves (Fig. 6) obtained by experiment. With alloys there is little change in resistance, as indicated in the curves (Fig. 7). The conductivity of carbon decreases with low temperatures, and increases with high ones. At the temperature of the electric arc carbon appears to have no resistance.

(To be continued.)

ON THE

DECOMPOSITION OF LIQUIDS BY CONTACT WITH POWDERED SILICA, &c.*

By Dr. G. GORE, F.R.S.

(Continued from p. 24).

On examining these results we find that by mere contact with the silica the *adhering* portion of the solution became stronger in ninety-seven instances, weaker in thirteen, and its strength was not perceptibly changed in the remaining thirty. The second group of cases may be regarded as those in which the silica united more strongly with the water than with the dissolved substance; and the third group may be considered either as those in which the amounts of dissolved substance or of water abstracted by the silica were too small to be detected by the method employed, or more probable that the two constituents of the liquid were abstracted in about the same proportion as they existed in the original solution. In all the various cases of alkaline solutions the *proportion* of dissolved substance abstracted was larger the greater the degree of dilution of the liquid.

We may regard the surface film of the liquid as being simply enlarged to a great extent by contact with the powder, and its solvent power being thereby usually increased, in which case the general results agree with a statement made by J. J. Thomson that, with saline solutions, in some cases the surface film of the liquid contains more and in others less salt per unit of volume than the interior ("Applications of Dynamics to Physics," p. 191); other circumstances, however, greatly affect the results. According to this view, in ninety-seven out of one hundred and forty instances the dissolved substance was more soluble in the capillary film than in the remaining mass of liquid.

Influence of Mixed Salts.

Water was added to 50 grains of silica, 38·75 of $MgCl_2$, and 38·75 of Na_2SO_4 until a total volume of 25·0 centims. of solution was attained. By means of volumetric analysis of the chlorine and gravimetric of the sulphuric acid it was found that whilst in No. 48 a 10 per cent solution of $MgCl_2$ alone gave a loss of 1·0 grain, or 2·6 per cent, in the present case there was no effect; and whilst a 10 per cent solution of Na_2SO_4 alone gave a gain of 0·42 grain, or 1·09 per cent (see No. 71), in the present instance there was a loss of 1·05 grains, or 2·8 per cent. With a solution containing 10 per cent *each* of KCl and K_2CO_3, analysed as in Nos. 1 and 76, after standing sixteen hours with 50 grains of silica, the KCl lost 4·68 grains = 12·17 per cent, and the K_2CO_3 lost 4·3 grains = 11·17 per cent, the loss in each case being increased by mixture (compare Nos. 91 and 113). These results show that salts in admixture disturb each other's effect.

Comparison of Filtration with Agitation and Subsidence.

The 0·025 per cent solution of KCy was filtered through 50 grains of the silica in a column 7½ inches high; it passed through in about one and half or two hours, and the first portion showed a loss of about 50·0 per cent. This was considerably less than that obtained by the ordinary method of agitation and subsidence (compare No. 114). Shaking, therefore, appears to promote the action.

Influence of Time.

The experiment with the 0·025 per cent solution of ammonium sesquicarbonate (see No. 131) was repeated, the period of digestion with the silica being only two hours. The proportion of salt abstracted was apparently the same as in the former case after four hours. The 0·25 per cent solution of KCy of No. 115 was also analysed after digestion of the silica in it during four hours and after sixteen hours, and the same result obtained in each case (compare notes of Nos. 117 and 118). The results show that prolonged digestion with the silica is unnecessary.

Influence of Strength of the Solution.

In the case of solutions which had an alkaline reaction, the actual amount of dissolved substance abstracted by the silica was nearly always greater, and the proportional amount nearly always less, the stronger the solution; but with solutions of acids or of neutral salts the effects were very variable. An inspection of the foregoing Table supports these statements.

Influence of Varying the Proportion of Silica.

Whilst the 25 c.c. of 10·0 per cent solution of potassic carbonate digested with 50 grains of silica during sixteen hours lost 3·12 grains, or 8·05 per cent (see No. 113), the same amount of the same solution digested with 100 grains of silica during the same period of time lost 4·16 grains, or 11·11 per cent. The amount of effect increased with the proportion of the silica.

Influence of Temperature.

The 1·0 per cent solution of potassic carbonate in contact with silica, which gave a loss of 1·02 grains = 26·6 per cent at atmospheric temperatures (see No. 111), lost 2·13 grains = 27·5 per cent at 140° F., each after a period of four hours' digestion; temperature, therefore, had but little effect. No silica was dissolved.

Influence of Kind of Solvent.

By employing a 1 per cent solution of NaCy in a mixture of equal volumes of water and absolute alcohol and the usual proportion of silica, a loss of 0·5 grain = 13·0 per cent of the salt occurred. This was a somewhat smaller effect than when the solvent was water alone. Compare No. 85. And by using a 1 per cent solution of K_2CO_3 in a similar manner, a loss of 1·22 grain = 31·7 per cent occurred, which was somewhat greater than with water alone as the solvent. Compare No. 111. The kind of solvent, therefore, has evidently an influence upon the effect.

(To be continued).

The People's Palace for East London. — Sir Benjamin Baker, K.C.M.G., F.R.S., has consented to distribute the Prizes and Certificates to the Evening-Class Studens at the People's Palace on January 24. The distribution will be combined with the Annual Conversazione to all the Evening Students. Sir John Johnson, Master of the Drapers' Company, will preside. The Evening Classes resumed work on the 8th instant.

* From the *Proceedings of the Birmingham Philosophical Society*, Vol. ix., Part I.

ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 9).

The refractive angle of these air-prisms was formed by the surface of the fluor-spar prism and the adjacent surface of the neighbouring lens. If the rays passed the fluor-spar prism symmetrically both the air-prisms were of equal size, and their refractive angle—if the line No. 31 was at the minimum of deflection—measured 59°. If the influence of these aërial prisms was considerable it was possible that even small variations of pressure in the apparatus might displace the image of the slit in the longitudinal direction of the prism and thus occasion the above-mentioned want of clearness in the lines.

Spectra situate below each other, one taken at the pressure of 760 m.m. and the other after exhausting the apparatus, with an unaltered position of the plate, showed in fact a very great displacement of the lines. The components of the line No. 31 differ from each other by 0·5 $\mu\mu$ in their wave-length, and the air-prisms have displaced the more refrangible of the two components by exactly so much, and the other lines in a proportion little different.

But before entering upon this matter I considered it advisable first to utilise the remaining results of absorption, those of gelatin and silver bromide, for the improvement of the photographic procedure hitherto employed, in order, if needful, to take their possible modification into consideration in re-modelling the apparatus.

(To be continued.)

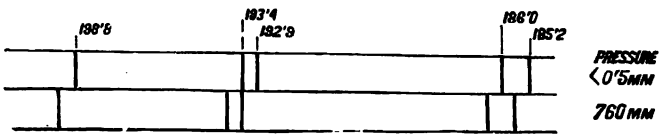


FIG. 4.

What applies to the prism holds good also for the lenses. Their focal distance is therefore greater in an apparatus filled with air than in one which has been exhausted. But I have not been able to show experimentally the connection between the focal distance and the atmospheric pressure, probably because my proofs were defective in the requisite clearness. This was the case even with great differences of pressure, and still more with the small fluctuations which here come into play.

But even the displacement of the lines by the air-prisms as they probably followed from the above-mentioned fluctuations of pressure was not sufficient—as appears at once from the proofs at the pressures of 0 and 760 m.m.—to explain the defective definition. In these circumstances the cause can be sought only in the other peculiarity of the vacuum apparatus, the two fluor-spar plates introduced into the rays. In their technical execution the plates were faultless. The optical surfaces were exact planes. But with the material the case seemed different. As already remarked fluor-spar is rarely homogeneous in large pieces. My plates were certainly of crystalline clearness at the point of transit of the rays, apparently purer even than the prism and the lenses.

But I infer that they were not free from faults in crystallisation from the fact that my proofs improved in clearness when I placed the sensitive plate, not, as hitherto, behind the fluor-spar plate, but close before it, *i.e.*, in the vacuum; and that also the removal of the other plate to before the slit acted in the same direction, though only to a slight extent.

This fact was more important for the continuation of my work than it might have been at first supposed. It required a profound reconstruction of my apparatus, in which exactly its most expensive parts, the production of which had engaged me for the longest time, had to be replaced by others.

* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 21st, 1893.

Dr. ARMSTRONG, President, in the Chair.

MESSRS. Frank Comyns, Martin O. Forster, Henry Garnett, and Arthur R. Ling were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of MESSRS. Walter Grafton, 11, Grosvenor Road, Upton Park, Essex; Robert Hamilton, 5, Lake Street, Hunslet, Leeds; W. Pellew Harvey, Golden, British Columbia; R. Hornby B.A., Long Preston, Leeds; Walter Jardine, 86, Victoria Place, Perth; Clifford Walker Lee, the Atacama Mineral Company, Taltac, Chili; John Peven, Jun., Blair Terrace, Greenock; A. B. Robertson, Dungoyne, Bearsden, by Glasgow; William Lloyd Williams, Erbistock Villa, 10, Miskin Road, Dartford.

The following is the text of a reply received by the President to his recent letter of congratulation to the Russian Chemical Society; the letter is signed by D. Mendeleeff, President, and D. Konowalow, Secretary, of the Society:—

"In the name of Russian chemists we tender to you our hearty thanks for the congratulations and the sentiments expressed by you in your letter of the 15th Nov., 1893, in the name of the London Chemical Society.

"The possibility, suggested by you, of a closer tie between the eminent London Chemical Society and the young Russian one was received with greatest applause. We hope, as well as you, that the time is not far off when this closer connection will take place. We desire it the more as we expect to gain the more by it."

Of the following papers those marked * were read:—

*91. "*Corydaline.* Part. III. *Oxidation with Potassium Permanganate.*" By JAMES J. DOBBIE, M.A., D.Sc., and ALEXANDER LAUDER.

By the oxidation of corydaline with potassium permanganate an acid is obtained which contains three atoms of carbon less than the alkaloid. This substance, which the authors have named corydalinic acid, has the formula $C_{19}H_{21}NO_{12}$. It is easily soluble in hot water, from which it separates, on cooling, in long, flat, prismatic crystals, containing 3 mols. of water of crystallisation. Corydalinic acid is also soluble in methyl and ethyl alcohol, but is insoluble in ether, chloroform, and benzene.

When heated, corydalinic acid sublimes without changing, and then condenses in the form of beautiful silky needles. It melts without decomposing between 175° and 180°.

Corydalinic acid is tetra-basic; the following salts have

been prepared and analysed:—A normal and acid silver salt, $C_{19}H_{17}NO_{12}Ag_4$ and $C_{19}H_{19}NO_{12}Ag_2$; an acid potassium salt, $C_{19}H_{19}NO_{12}K_2$; a normal and acid barium salt, $C_{19}H_{17}NO_{12}Ba_2$ and $C_{19}H_{19}NO_{12}Ba$; and the normal lead salt, $C_{19}H_{17}NO_{12}Pb_2$.

The acid silver salt, when carefully heated, yields a beautiful sublimate of corydalinic acid. The normal silver and barium salts are appreciably soluble in water; the lead salt is almost insoluble.

When treated with fuming iodhydric acid, one molecular proportion of corydalinic acid gives four molecular proportions of methyl iodide, showing that the four methoxy groups which corydaline contains are still present in the acid. The formula of the acid may, therefore, be written $C_{11}H_5N(OCH_3)_4(COOH)_4$.

Corydalinic acid is split up into a number of simpler substances by the action of fuming iodhydric acid. Of these, the one which is formed in largest quantity is a non-nitrogenous acid, which crystallises from the iodhydric solution in long, slender, colourless needles. The formula of this acid, which the authors temporarily name corydalic acid, is $C_9H_{10}O_8$. When heated, corydalic acid melts at 200°, undergoing decomposition. It is a powerful reducing agent: when silver nitrate is added to its aqueous solution a white precipitate is obtained, which partially dissolves on heating, and is partially reduced, silver separating; in presence of ammonia the reduction is instantaneous, even in the cold. Copper acetate is rapidly reduced to cuprous oxide on heating with an aqueous solution of the acid. Ferric chloride colours solutions of the acid intense green, the colour changing to violet on the addition of ammonia or sodium carbonate. A phenol is evolved when corydalic acid is heated with lime.

The authors experienced great difficulty in obtaining definite salts of corydalic acid, partly on account of the ease with which some of them decompose, and partly because of the difficulty of ascertaining the precise conditions under which the acid and normal salts respectively can be obtained. A lead salt of the formula $C_9H_6O_8Pb_2$ was prepared, as well as a salt containing a larger proportion of lead.

Corydalic acid appears to be a dihydroxytricarboxylic derivative of a reduced benzene ring, the hydrogen both of the hydroxyl and carboxyl groups being displaceable by metal, as in the case of other phenolic acids.

The mother-liquors from corydalic acid contain several substances, including a nitrogenous compound, which have not yet been investigated.

The authors consider it probable that corydalinic acid is a derivative of phenylpyridine, in which three carboxyl- and two methoxy-groups are united to a partially-reduced benzene ring and one carboxyl- and two methoxy-groups to the pyridine ring. The formation of such an acid from corydaline would be most easily accounted for by the assumption that corydaline is itself a derivative of a naphthaquinoline. Corydalinic acid would thus be obtained from corydaline in the same manner as phenylpyridinedicarboxylic acids are obtained by the oxidation of the naphthaquinolines.

If is further probable that the three carbon atoms of corydaline which are split off during oxidation are attached to the benzene ring, and are represented by two of the three carboxyl groups present in this portion of the acid.

Corydaline is very stable towards potassium hydrate, only a small portion of the alkaloid undergoing alteration, even when heated at 180° during many hours with a large excess of this agent.

"92. "*The Properties of α-Benzaldoxime and some of its Derivatives.*" By Wyndham R. Dunstan, F.R.S., and C. M. Luxmoore, B.Sc.

The authors wish to place on record certain facts they have observed during the course of an investigation of the isomerism of the benzaldoximes which is not yet completed.

Crystallisation of α-Benzaldoxime.—More than a year ago they observed that α-benzaldoxime, which had been described by Petraczek, Beckmann, Hantzsch, and previous observers, as a yellowish oil, could be crystallised by cooling, with ice and salt, the colourless highly-refractive liquid obtained by distilling the yellow oil under reduced pressure. The substance is best recrystallised from its solution in light petroleum. The crystals melt at 34°. Both the isomeric benzaldoximes are, therefore, crystalline compounds, the β-oxime melting at 129°. As the result of a considerable experience in the preparation of the α-compound the authors find the method suggested by Beckmann, in which the aldehyd is acted on by hydroxylamine, to be preferable to that proposed by Lachowitz (*Ber.*, xxii., 2887), namely, the interaction of hydrobenzamide and hydroxylamine hydrochloride.

Action of Hydrogen Chloride on α-Benzaldoxime.—Beckmann has shown that hydrogen chloride, as well as hydrogen sulphate, converts α-benzaldoxime into the isomeric β-benzaldoxime. The authors also find that, when the α-compound or its ethereal solution is charged with dry hydrogen chloride at the ordinary temperature, the hydrochloride of β-benzaldoxime is obtained, separating from the ethereal solution in pearly crystals which melt at 66—67°. This compound is best re-crystallised from its solution in chloroform by the cautious addition of light petroleum. When dissolved in water at 0° it dissociates into hydrogen chloride and β-benzaldoxime (which may be recovered by means of ether). If, however, the mixture be allowed to stand, especially at the ordinary temperature, the dilute acid quickly transforms the β-oxime into the α-oxime. Dry hydrogen chloride and aqueous hydrogen chloride, under the same conditions, tend therefore to induce isomeric change in opposite directions; the dry gas at ordinary temperatures changing the α-compound into the β-compound, whilst the aqueous acid, under similar circumstances, changes the β- into the α-compound.

Hantzsch did not succeed in producing a hydrochloride of α-benzaldoxime. The authors have obtained this substance by leading dry hydrogen chloride into an ethereal solution of the α-compound, well cooled below 0°, any rise in temperature being avoided. It is thrown down as a pulverulent precipitate melting somewhat indefinitely near 103°. When dry it appears to be perfectly stable at the ordinary temperature, but on attempting to crystallise it from chloroform isomeric change takes place, and the hydrochloride of the β-benzaldoxime is obtained, When acted on by dilute aqueous ammonia at 0° the α-hydrochloride furnishes the α-oxime.

Action of Hydrogen Bromide and Hydrogen Iodide.—Neither the hydrobromide nor the hydriodide of α-benzaldoxime could be isolated. Even at temperatures below 0°, when these gaseous hydrides are led into an ethereal solution of the oxime, the hydrobromide and the hydriodide of β-benzaldoxime are produced. The *hydrobromide* ($C_6H_5CH{:}NOH$) melts at 77—78°; the *hydriodide* is unstable, decomposing on standing, iodine being liberated.

Action of Hydrogen Fluoride. — No hydrofluoride of α benzaldoxime could be obtained. Hydrogen fluoride throws out from an ethereal solution of the oxime, cooled below 0°, a salt which proved, on analysis, to be the *dihydrofluoride* of β-benzaldoxime—

$$(C_6H_5CH:NOH{\cdot}2HF).$$

Action of Sulphuric Acid.—Beckmann observed that when benzaldoxime is dissolved in concentrated sulphuric acid, and the solution is poured into water at 0°, the isomeric β-benzaldoxime results. The authors find that the isomeric change, as in the similar case of hydrogen chloride, is preceded by the formation of an unstable *α-benzaldoxime sulphate*, which may be prepared, as an oil, by mixing α-benzaldoxime with an ethereal solution of sulphuric acid cooled to about −15°. Dilute aqueous

ammonia acting at 0° regenerates α-benzaldoxime from this compound. The oily salt very readily undergoes isomeric change into solid β-benzaldoxime sulphate. On standing, or on vigorously stirring the liquid cooled to 0°, solidification occurs owing to the formation of *β-benzaldoxime sulphate* ($C_6H_5CH:NOH,H_2SO_4$), which furnishes β-benzaldoxime when decomposed at 0° with dilute aqueous ammonia.

Crystallisation of Acetyl-α-Benzaldoxime.—This compound has hitherto been regarded as an oil. It can, however, when pure, be crystallised by vigorously stirring the liquid cooled below 0°. The crystals melt between 14° and 16°. Both the acetyl-α-benzaldoxime and the acetyl-β-benzaldoxime are, therefore, crystalline solids.

Action of Alkyl Haloids.—Methyl bromide, and apparently other alkyl haloids, act on α-benzaldoxime, furnishing crystalline derivatives, which the authors are investigating.

*93. "*The Interaction of Acid Chlorides and Nitrates.*" By Henry E. Armstrong and A. Lapworth.

It was shown by one of the authors in 1873 (*Chem. Soc. Journ.*, p. 683) that acetic chloride and nitrates interact, forming acetic oxide, and that a mixture of chlorine and nitric peroxide gases is evolved instead of the compound NO_2Cl, which at that time was supposed to be capable of existing: it was suggested that in the case of silver nitrate perhaps the initial change involved the formation of silver acetate, chlorine, and nitric peroxide, and that silver chloride and acetic oxide were then formed by the interaction of the silver acetate and acetic chloride. These observations were confirmed in 1886 by W. C. Williams (*Chem. Soc. Trans.*, p. 222), in so far as the production of chlorine and nitric peroxide was concerned, but Lacowicz had meanwhile stated (*Ber.*, 1884, 1281; 1885, 2990) that the gaseous products of such interchanges are nitric peroxide and oxygen, a result which was not confirmed by Williams.

The authors have extended the observations in order to throw further light on the evolution of chlorine in such cases, and with the object of elucidating the function of chlorine in acid chlorides (*cf. Proc. Chem. Soc.*, 1891, 60). By displacing the air from the apparatus by carbon dioxide, and then passing the evolved gases first through oil of vitriol and afterwards through alkali contained in an apparatus such as is used in determining nitrogen, they have satisfied themselves that only chlorine and nitrogen peroxide are evolved. Quantitative experiments show that in the case of silver nitrate and acetic chloride half the chlorine is evolved and half retained as metallic chloride; but it would seem that chloride is only produced when the chloride used is capable of acting on the salt which is formed in the initial interaction: thus chlorosulphonic acid, $ClSO_3H$, and potassium nitrate afford little or no chloride, the nitrate being converted into acid sulphate. The results of experiments with a variety of acid chlorides and nitrates appear to justify the conclusion that the interaction is one involving the mere displacement of the chlorine of the chloride by oxygen from the nitrate; and, in point of fact, nitric anhydride is found to act in the manner to be expected on this assumption, at once converting acetic and benzoic chlorides into the corresponding oxides, chlorine and nitric peroxide. As nitric peroxide has no action on silver nitrate, and as nitrylic chloride has no existence, the formation of nitric anhydride by Deville's method must be considered to be a direct outcome of the interaction of silver nitrate and chlorine; and if silver nitrate be regarded as a compound of the formula $Ag_2O{\cdot}N_2O_5$—a view on behalf of which much may be said—it is conceivable that chlorine simply acts on the "silver oxide radicle," removing it from combination with the nitric anhydride, and consequently liberating the latter. The results obtained appear generally to support the conclusion that the chlorine in acid chlorides is not possessed of the special activity which is commonly attributed to it.

*94. "*The Freezing-points of Triple Alloys.*" By C. T. Heycock and F. H. Neville.

Continuing their experiments on the freezing-points of alloys, the authors find that gold and cadmium, which in previous experiments seemed to combine together to form a compound (AuCd), behave similarly when they are together dissolved in tin, bismuth, thallium, or lead. The interaction of these metals appears, therefore, to be independent of the nature of the solvent.

Silver and cadmium, when dissolved together in different metallic solvents, give results resembling those obtained with gold and cadmium. Dissolved in tin or lead the maximum freezing-point is reached when the ratio of the two metals is 2Ag : Cd, and in thallium the ratio is almost the same. With bismuth, however, the maximum freezing-point is reached at the proportion 4Ag : Cd. The existence of metallic compounds having these formulæ seems to be probable.

Aluminium, when dissolved with tin and gold, behaves as if it were composed of molecules of the composition Al_2. The maximum freezing-point of a mixture of aluminium and tin to which gold has been added is identical with that of pure tin, and corresponds with the proportion $Al_2Au_{0\cdot9}$. It appears probable from these results that a stable, insoluble compound ($AuAl_2$) is produced, the gold completely removing the aluminium from solution. This compound is apparently identical with Roberts-Austen's purple alloy of aluminium and gold.

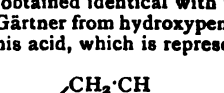
*95. "*Synthesis of Pentamethylenecarboxylic Acid, Hexamethylenecarboxylic Acid, Hexhydrobenzoic Acid, and Azelaic Acid.*" By E. Haworth, B.Sc., and W. H. Perkin, jun., F.R.S.

With the object of preparing hexhydrobenzoic acid synthetically by the interaction of pentamethylene dibromide and ethylic sodiomalonate, the authors followed the directions given by Gustavson and Demjanoff (*J. Pr. Chem.*, xxxix., 542) for the preparation of the dibromide from the diamine obtained by reducing trimethylene cyanide; they obtained from 1500 grms. of trimethylene bromide only 90 grms. of what was supposed to be pentamethylene bromide, but which, judging from the results obtained with it, chiefly consisted of tetramethylene bromide. The main product of the interaction of this bromide and ethylic sodiomalonate was 1 : 1-pentamethylenedicarboxylic acid, $C_5H_8(CO_2H)_2$. On distilling this acid, a monocarboxylic acid was obtained which was identified by direct comparison with that prepared by Wislicenus and Gärtner from the cycloid ketopentamethylene produced from adipic acid.

By distilling the oil from which the pentamethylenedicarboxylic acid had crystallised out a higher fraction was obtained consisting of hexamethylenecarboxylic acid, which proved to be identical with the hexhydrobenzoic acid prepared by Aschau from benzoic acid.

In addition to the two dicarboxylic acids derived from tetra- and penta-methylene bromides respectively and a single molecular proportion of malonate, a tetracarboxylic acid was also isolated which was derived from 1 mol. of pentamethylenebromide and 2 of malonate; on distillation, this acid was resolved into carbon dioxide and a heptanedicarboxylic acid which proved to be identical with azelaic acid prepared by oxidising Chinese wax.

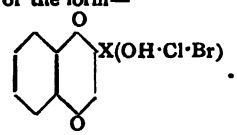
By brominating pentamethylenecarboxylic acid and then removing hydrogen bromide, a pentamethenylenecarboxylic acid was obtained identical with that prepared by Wislicenus and Gärtner from hydroxypentamethylenecarboxylic acid. This acid, which is represented by the formula—



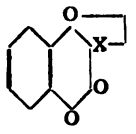
resembles benzoic acid in appearance, and not only has the same melting-point, but also sublimes with great readiness.

*96. "*The Conversion of Ortho- into Para-, and of Para- into Ortho-quinone Derivatives. I. The Condensation of Aldehyds with β Hydroxy-α-naphthaquinone.*" By S. C. Hooker and W. C. Carnell.

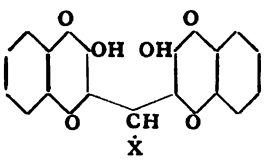
Attention has been directed in previous communications on lapachol-derivatives to the formation of anhydrides by the removal of water or of hydrogen chloride or bromide from compounds of the form—



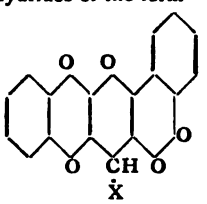
It was found that the majority of the lapachols gave two isomeric anhydrides, the one an α-, the other a β-naphthaquinone derivative, while a few have afforded but a single anhydride derived from the β-quinone. In order to ascertain whether anhydrides of the form—



are generally produced, the authors have studied the behaviour of compounds synthetically prepared from aldehyds and β-hydroxy-α-naphthaquinone, such as were first obtained by Zincke and Thalen (*Ber.*, xxi., 2203). From some of these, small quantities of anhydrides were obtained by Schooch. The authors' experiments show that the conclusions arrived at by Zincke and his pupils that these anhydrides were α-quinone derivatives was incorrect, and that—as was to be anticipated from the results arrived at in the course of the lapachol research—they are in reality β-quinone derivatives, the formation of the anhydride also involving the passage of the α- into the β-quinone. It would appear probable that the compounds of the form—



derived from aldehyds and hydroxy-α-naphthaquinone are converted into anhydrides of the form—



as when brought into contact with orthotoluylenediamine these anhydrides afford only *mon*azines. It has been shown that in the lapachol group both the α- and β-anhydrides are readily hydrated, and yield the same hydroxylapachol, a change which, in the case of the β-anhydrides, involves the re-conversion of the ortho- into the para-quinone; the synthesised anhydrides behave similarly, but the change is more difficult to demonstrate, as the hydroxy derivatives very rapidly undergo change in contact even with very dilute caustic soda—an interaction which is being studied in detail. The compounds dealt with are those derived from benzaldehyd, acetaldehyd, valeraldehyd, and cuminic, salicylic, and cinnamic aldehyds: in all cases the anhydrides obtained were orange or red compounds, yellow being the colour characteristic of the α-anhydride.

*97. "*The Synthesis of Lapachol.*" By S. C. Hooker.

By heating hydroxynaphthaquinone dissolved in acetic acid together with valeric aldehyd and concentrated chlorhydric acid, the author has obtained an isomeride of lapachol crystallising in orange-red needles, which melts at 119—120°, and forms violet-coloured salts with alkali metals; its acetate melts at 74°. From this compound others have been obtained containing the same number of carbon atoms as lapachol, and identical with substances prepared from lapachol.

NOTICES OF BOOKS.

Dictionary of the Active Principles of Plants. Alkaloids, Bitter Principles, Glucosides: their Sources, Nature, and Chemical Characteristics, with Tabular Summary, Classification of Reactions, and Full Botanical and General Indexes. By Charles E. Sohn, F.I.C., F.C.S., Member of Society of Public Analysts. London: Baillière, Tindall, and Cox. 1894.

This work, on examination, appears calculated to be so exceedingly useful that we are surprised that it has not been long ago anticipated. Yet to our best knowledge nothing similar has yet appeared.

The first portion of the book gives the plants concerned in alphabetical order, with the botanical order to which each belongs, the names of the chemists by whom it has been investigated, and the source of their original memoirs. Then follow the names and the composition of their active principles, their solubilities, and reactions. Thus, under *Ruta graveolens* (rue) we find its order, the *Rutaceæ*, its sources, *i.e.*, capers, Chinese yellow berries, safflower, *Polygonum fagopyrum*, &c. The principles contained are rutine, $C_{25}H_{28}O_{15}+2\frac{1}{2}H_2O$, with its solubilities and reactions, and sophorin.

The second part of the work is the practical summary. For the full details of tests for any one substance the reader is referred to Part I., and for other substances giving similar reactions to Part III. We find in parallel columns the name of its substance, its formula, appearance or crystalline form, melting-point, reaction, taste, solubility in water, alcohol, ether, chloroform, special solvents, behaviour with caustic alkalis, lead acetate, tannic acid, platinum chloride, gold chloride, sulphuric acid (concent.), nitric acid (concent.), and behaviour with special reagents, such as Fehling's solution, Mayer's solution, Frœhde's test, &c.

Part III. gives the solubilities in water, alcohol, ether, the substances precipitated by and soluble or insoluble in caustic alkalis, behaviour with lead acetate, with tannic acid, picric acid, ferric chloride, platinum chloride, gold chloride, silver nitrate, Fehling's solution, potassium ferrocyanide, ferricyanide, sulphocyanide, chromate, bichromate, phospho-molybdic acid, phospho-tungstic acid (Scheibler's reagent), phospho-antimonic acid (Schultz's reagent), iodo-potassic iodide (Wagner's solution), bismuth potassic iodide (Dragendorff's reagent), cadmium potassic iodide (Marmé's reagent), zinco-potassic iodide, mercuric potassic iodide (Mayer's solution), mercuric chloride, &c. Then follow the botanical index and the general index, with certain addenda.

We are convinced that chemists engaged in research, analysts, toxicologists, pharmacists, and manufacturers will find this book a great assistance. It will often save them untold time and trouble.

On Viscosimeters for Oils.—Certain improvements have been devised bearing upon the accuracy of the arrangements. The apparatus cannot be intelligibly described without the figure.—*Zeitschrift f. Angewandte Chemie.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 1, January 2, 1894.

This issue shows the present arrangement of the Academy of Sciences. In the section for geography there is one vacancy, as also in that for rural economy. The two perpetual secretaries are J. L. F. Bertrand, for the mathematical sciences, and M. P. E. Berthelot, for the physical sciences. It is noteworthy that physics does not rank among the physical sciences, and that geography is placed in the mathematical department. In addition to the two perpetual secretaries already mentioned, there is a perpetual honorary secretary, the illustrious Pasteur. There are, besides the members of the sections, a number of "free academicians" not supposed to be especially connected with any one science, and seven foreign associates, including Lord Kelvin and Sir J. Lister. The correspondents are a numerous and highly distinguished body. Among the normal academicians—if we may so call them—only two have escaped the decoration of the Legion of Honour.

Chemical Study on the Nature and the Causes of the Green Colouration in Oysters.—Ad. Chaten and A. Muntz.—This question is at once chemical and biological. The investigation has been committed to a M. Berthelot (probably a son of the M. Berthelot), of the Academy of Sciences. It is shown that the green colour of oysters has no relation with the chlorophyll of plants, or with other known colouring matters, animal or vegetable. He shows also that oysters contain iron, and that the mud of the oyster beds contains iron sulphide, to which its black colour is owing. Both the colouring matter and the iron are especially accumulated in the gills of the oysters, whilst the rest of the body is nearly colourless. The composition of the green pigment has not been determined.

New Isomer of Cinchonine.—E. Jungfleisch and E. Léger.—On acting with alcoholic potassa upon hydrobromocinchonine bihydrobromate, there are produced cinchoniline, cinchonifine, apocinchonine, and a little of cinchonine δ, the novel base in question. If allowed to crystallise from ether it forms elongated prisms. It is insoluble in water, freely soluble in alcohol, benzene, chloroform, and acetone. It melts at 150°. It is dextrorotatory. Its rotatory power (determined at 17° in a 1 per cent solution in alcohol at 97 per cent) is $\alpha_D = +125{\cdot}2°$. If dissolved in 100 parts of water with the addition of 2HCl it gives $\alpha_D = 176{\cdot}9°$, and with an addition of 4HCl $\alpha_D = +178{\cdot}2°$. Cinchonine δ in the free state or in its salts gives solutions which change colour quickly on exposure to air and light, forming brown products much less alkaline than the base itself. The salts of cinchonine δ are in general very soluble in water; but the hydrochlorate, the hydrobromate, and the oxalate (basic) are sparingly soluble in the cold, and crystallise readily.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Liquid Chlorine.—Could you kindly oblige by letting me know who or what firm are manufacturing liquid chlorine, or from what source I could obtain any?—W.

Liquid Chlorine.—We have seen in a foreign contemporary a note that liquid chlorine gas is now prepared in Europe on a large scale for chemical works. The gas is liquefied by a special pump, and is transported in steel cylinders. Could you kindly tell us whether this is within your knowledge, and whether you know of any manufacturers or chemical works at home or abroad producing or using chlorine in such form? Any information on the subject would be esteemed.—Editor.

MEETINGS FOR THE WEEK.

Monday, 22nd.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "The Detection and Measurement of Inflammable Gas and Vapour in the Air," by Frank Clowes, D.Sc.
Tuesday, 23rd.—Royal Institution, 3. "Locomotion and Fixation in Plants and Animals," by Prof. Charles Stewart, Pres.L.S.
—— Medical and Chirurgical, 8.30.
—— Institute of Civil Engineers. 8.
—— Photographic, 8.
—— Society of Arts, 8. "Morocco and its Races," by Capt. Charles Rolleston.
Wednesday, 24th.—Society of Arts, 8. "American Carriages," by G. Herbert Thrupp.
—— Geological, 8.
Thursday, 25th.—Royal, 4.30.
—— Royal Institution, 3. "The Life and Genius of Swift," by the Rev. Canon Ainger, LL.D.
—— Institute of Electrical Engineers, 8.
Friday, 26th.—Royal Institution, 9. "Old Irish Song," by Alfred Perceval Graves, M.A.
—— Physical, 5. "A New Mode of Making Magic Mirrors," by J. W. Kearten. "Some Observations in Diffraction," by W. B. Croft, M.A. "A New Photometric Method and Photometer," by J. W. Spurge.
Saturday, 27th.—Royal Institution, 3. "English Schools of Musical Composition," by Prof. W. H. Cummings.

Erratum.—P. 5, col. 1, in the Table headed "English Committee," Phosphorus, Standard No. 4, *for* "0·178" *read* "0·078."

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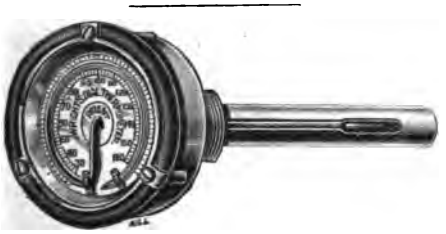

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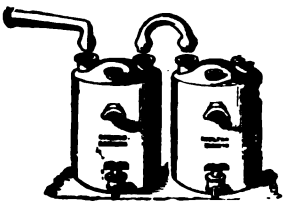

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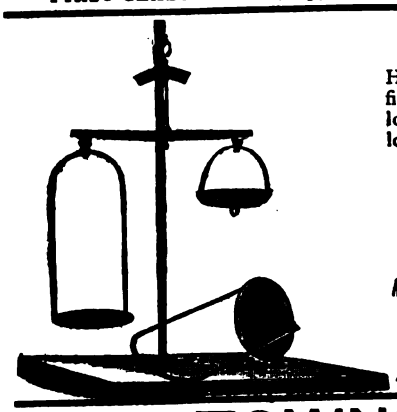

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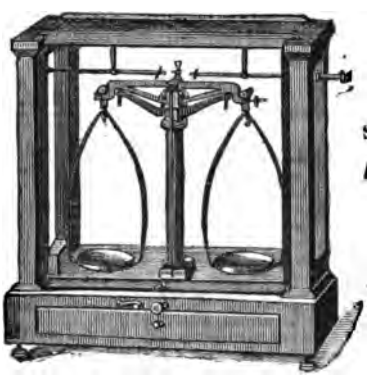

FIG. 3a.

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THE CHEMICAL NEWS.

Vol. LXIX., No. 1783.

LIQUID ATMOSPHERIC AIR.*

By Professor DEWAR, M.A., LL.D., F.R.S.

(Concluded from p. 33.)

The optical constants of liquid oxygen, ethylene, and nitrous oxide have been so far determined, and in this matter my colleague, Professor Liveing, has been associated with me in the conduct of this work. The results obtained are given in the following table, and tend to confirm the law of Gladstone as being applicable to such substances:—

Refractive Indices of Liquid Gases.

	Index.	Ref. constant.	Ref. molecular
Oxygen	1·2236	1·989	6·364
Ethylene	13632	0·626	17·528
Nitrous oxide ..	13305	0·263	11·587

Law of Gladstone $\frac{\mu - 1}{D}$ = constant.

The determination of the refractive index of liquid oxygen at its boiling-point of −182° C., presented more difficulty than would have been anticipated. The necessity for enclosing the vessel containing the liquid in an outer case to prevent the deposit of a layer of hoar-frost which would scatter all the rays falling on it, rendered manipulation difficult; and hollow prisms with cemented sides cracked with the extreme cold. It was only after repeated attempts, involving the expenditure of a whole litre of liquid oxygen on each experiment, that we succeeded in getting an approximate measure of the refractive index for the D line of sodium. The mean of several observations gave the minimum deviation with a prism of 59° 15′ to be 15° 11′ 30″, and thence $\mu = 1{\cdot}2236$. The density of liquid oxygen at its boiling-point of −182° C. is 1·124, and this gives for the refraction constant,—

$$\frac{\mu - 1}{d} = 1{\cdot}989,$$

and for the refraction-equivalent 3·182. This corresponds closely with the refraction-equivalent deduced by Landolt from the refractive indices of a number of organic compounds. Also it differs little from the refraction-equivalent for gaseous oxygen, which is 3·0316. This is quite consistent with the supposition that the molecules of oxygen in the liquid state are the same as in the gaseous.

If we take the formula—

$$\frac{\mu^2 - 1}{(\mu^2 + 2)\,d}$$

for the refraction-constant we find the value of it for liquid oxygen to be 0·1265, and the corresponding refraction-equivalent 2·024. These are exactly the means of the values found by Mascart and Lorenz for gaseous oxygen. The inherent difficulties of manipulation, and the fact that the sides of the hollow prism invariably became coated with a solid deposit, which obscured the image of the source of light, have hitherto prevented our determining the refractive indices for rays other than D.

The optical projection of vacuum vessels having the shape of a double test-tube are very suitable for lecture illustration. As the critical point of oxygen is some thirty degrees higher than nitrogen it is easier to liquefy, and, consequently, becomes the most convenient substance to use for the production of temperatures about −200° C. Liquid nitrogen, carbonic oxide, or air can conveniently be made at the ordinary atmospheric pressure, provided they are brought into a vessel cooled by liquid oxygen boiling under the pressure of about half an inch of mercury.

A simple arrangement for this purpose is shown in Fig. 8. The inner tube contains the liquid oxygen under exhaustion, surrounded by a vacuum vessel, the interior space between the inner tube and the vacuum vessel being connected with a receiver containing the gas which

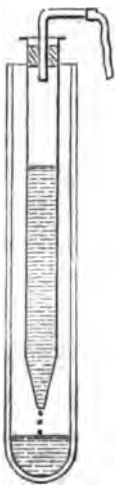


Fig. 8.

is to be liquefied. If the object is to collect liquid air the inner air space is left quite open, no precautions being needed to free the air from carbonic acid or moisture, because under the conditions such substances are solids, and only cause a slight opalescence in the liquid, which drops continuously from the end of the inner tube and accumulates in the vacuum vessel. If the air supply is forced to bubble through a little strong sulphuric acid, the rate of condensation and the relative volume of gas and liquid can be observed, Liquid air boils at the temperature of −190° C., giving off substantially pure nitrogen. As the nitrogen boils 10° C. lower than oxygen,

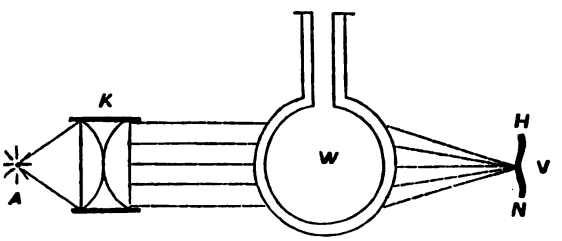


Fig. 9.

after a time the liquid alters its composition and boiling-point, finally becoming pure oxygen. During the evaporation the liquid air changes very remarkably in colour, passing from a very faint blue to a much deeper shade. The changes can be traced best by the marked increase in the width of the absorption bands of liquid oxygen. If air, collected in the above manner in a vacuum vessel, is isolated from a rapid heat supply by immersing the vessel in liquid oxygen, and then a powerful air-pump brought to act upon it, after a time it passes into the condition of a clear, transparent, solid ice.

* A Lecture delivered before the Royal Institution of Great Britain, Friday, January 20, 1893. (We are indebted to *The Engineer* for the loan of the woodcuts illustrating this article).

Nitrogen solidifies, under such conditions, into a white mass of crystals, but all attempts to solidify oxygen by its own evaporation have failed. Such liquids as air and oxygen, we should anticipate, would be especially transparent to heat radiation, seeing they are very diathermic substances in their gaseous state. The thermal transparency of liquid oxygen can be shown by passing the radiation from the electric arc, as shown in the diagram, through a spherical vacuum vessel filled with clear filtered iquid; thereby concentrating the rays at a focus and igniting a piece of black paper held there.

In this experiment the oxygen lens has a temperature of −180° C., yet it does not prevent the concentrated radiation reaching a red heat at the focus. At such low temperatures as boiling oxygen and air all chemical action ceases. If some liquid oxygen is cooled to −200° C., and a glowing piece of wood inserted into the vessel above the liquid, it refuses to burst into flame, because of the low pressure of the vapour. An interesting experiment may be made by immersing an electric pile, composed of carbon and sodium, into liquid oxygen, when almost immediately the electric current ceases. The gaseous oxygen coming from the liquid must be exceedingly pure and dry, and as it has been alleged two chemical substances require the presence of a third one in order that they may combine, it was interesting to ascertain if a substance like sulphur would continue to burn after ignition in such an atmosphere. Sulphur placed in a small platinum vessel that had just been heated to redness, was raised to the boiling-point, and in the act of combustion lowered into a vacuum vessel containing liquid oxygen. The combustion continued active, and for a time could be maintained in the middle of the liquid oxygen. This result suggests that oxygen and sulphur can enter into combination in a perfectly dry condition. Some notion of the temperature of liquid air is given by running on to the surface some absolute alcohol, which, after rolling about in the spheroidal state, suddenly solidifies into a hard transparent ice, which rattles on the sides of the vacuum testtube like a marble. On lifting the solid alcohol out by means of a looped wire the application of the flame of a Bunsen burner will not ignite it. After a time the solid melts and falls from the looped wire like a thick syrup.

It is not the question of the change of state in matter, however interesting, that in our day has special attractions for the chemist, but the means of studying the properties of matter generally under the conditions of such exceptionally low temperatures as are the concomitants of the transition in the case of substances like oxygen and nitrogen. The work of investigation in this field proceeds slowly but surely, and one need not despair (unless on the grounds of expense) in the future of adding further data to our knowledge of the properties of matter near the zero of absolute temperature.

At the commencement of the lecture reference was made to the dangers and difficulties of this kind of research, and it becomes a pleasant duty to acknowledge the great services rendered by my assistants. But for the persistency and determination of Mr. Lennox, coupled with his marked engineering ability, the work would not have made such progress, and he has been ably supported by Mr. Heath.

Institute of Chemistry of Great Britain and Ireland.—Pass List of the Examination held at the Laboratories at 30, Bloomsbury Square, on Monday, January 8, 1894, and following days.—The following nine candidates were successful:—J. H. Baker, Finsbury Technical College, London; F. S. Bayley, Finsbury; F. B. Burls, Finsbury; J. Chilwell, Mason College, Birmingham; J. Hanley, University College, Liverpool; H. R. Lesueur, University College, London; G. E. Shaw, student under Mr. David Howard, F.I.C., and at Finsbury; and F. Southerden, Finsbury.

THE POLARISCOPE IN RELATION TO CHEMICAL CONSTITUTION.*

By PERCY FRANKLAND, Ph.D., B.Sc. (Lond.), F.R.S., Professor of Chemistry in University College, Dundee, St. Andrews University.

(Concluded from p. 29).

Recent Additions to our Knowledge of Asymmetric Carbon Atoms.

SPECULATION concerning the asymmetric carbon atom and the optical activity to which it gives rise has, however, recently been carried still further.

All who have used the polarimeter are aware that different active substances rotate the plane of polarisation through different angles, and the apparently anomalous circumstance is not unfrequently observed of a simple derivative of an active substance rotating the plane of polarisation in the opposite direction to that of the parent substance. This phenomenon is well exhibited by the following series.

	$[\alpha]_D$.
Diacetyltartaric acid	−23·14°
Methyl salt of diacetyltartaric acid ..	−14·29
Ethyl ,, ,, ,, ..	+ 1·02
Propyl ,, ,, ,, ..	+ 6·52
Isobutyl ,, ,, ,, ..	+10·29

A most ingenious attempt has recently been made by Crum Brown and Guye to account for these quantitative relations between the rotatory power of different substances by taking into consideration the respective weights of the four groups which are attached to the asymmetric carbon atoms, and arguing that the more nearly equal in weight two of these groups become, the more nearly will optical inactivity be approached, whilst the greater the disparity in weight of the groups, the greater should the activity be.

These points are exemplified by a series of derivatives of active glyceric acid which I have recently prepared in conjunction with Mr. John MacGregor, and which exhibit the following rotations:—

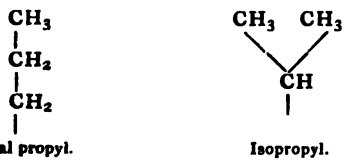
	Weights of groups attached to asymmetric carbon atom.	Specific rotation. $[\alpha]_D$.
Methyl glycerate	H=1, HO=17, CH_2OH=31, $COOCH_3$=59.	− 4·80°
Ethyl glycerate	H=1, HO=17, CH_2OH=31, $COOC_2H_5$=73.	− 9·18
Propyl (normal) glycerate ..	H=1, HO=17, CH_2OH=31, $COOC_3H_7$=87.	−12·94
Butyl (normal) glycerate ..	H=1, HO=17, CH_2OH=31, $COOC_4H_9$=101.	−13·19

Thus, whilst three out of the four groups attached to the asymmetric carbon atom remain constant, the fourth group increases in weight from 59 to 73 to 87 to 101, concurrently with which increase the rotatory power increases also.

In order to put this theory to the test it is obviously of interest to ascertain what is the effect of replacing one of these groups by another group of equal weight; thus, in the series above, in addition to normal propyl glycerate, we have also prepared isopropyl glycerate, and found its specific rotation to be less than that of the normal, viz., −11·82°. Thus it would appear that the masses of the groups are not necessarily attached directly to the corners of the tetrahedron, but that the centres of gravity of the groups may be at different distances from the corners of the tetrahedron depending upon the internal structure of the groups themselves. Thus, in the case in point this

* A Paper read before the North of England Institute of Technical Brewing, Manchester, Oct. 20th, 1893.

difference in the distance of the centres of gravity of the normal and isopropyl groups is plausibly explicable on the generally acknowledged views concerning their structure; thus the material interpretation of the formulæ—



Normal propyl. Isopropyl.

would indicate that the centre of gravity of the normal propyl should be further from the point of attachment than that of the isopropyl.

There are, however, other cases which find no such ready explanation by this theory, and which lead us to conclude that the theory will have to be materially modified before it embraces all known facts. Thus I have recently prepared in conjunction with Mr. MacGregor the following derivatives of active glyceric acid, which exhibit some very interesting relations:—

	Specific rotation. $[\alpha]_D$.
Methyl glycerate— 1. H=1. 2. HO=17. 3. CH_2OH=31. 4. $CH_3O.CO$=59.	− 4·80°
Methyl diacetylglycerate— 1. H = 1. 2. $CH_3CO.O$ = 59. 3. $CH_3CO.OCH_2$=73. 4. $CH_3O.CO$=59.	− 12·04
Ethyl diacetylglycerate— 1. H = 1. 2. $CH_3CO.O$ = 59. 3. $CH_3CO.OCH_2$=73. 4. $CH_3CH_2O.CO$ =73.	− 16·31
Propyl diacetylglycerate— 1. H = 1. 2. $CH_3CO.O$ = 59. 3. $CH_3CO.OCH_2$=73. 4. $CH_3CH_2CH_2O.CO$=87.	− 19·47
Isobutyl diacetylglycerate— 1. H = 1. 2. $CH_3CO.O$ = 59. 3. $CH_3CO.OCH_2$=73. 4. $\begin{matrix}CH_3\\CH_3\end{matrix}>CH$ $CH_2O.CO$=101.	− 20·48

In this series it will be seen that we have the most interesting relationships between the masses or weights of the groups attached to the asymmetric carbon atoms. Thus we start with a compound in which all the groups are of different weight, and in the order—

(1) < (2) < (3) < (4)

this is followed by—

(1) < (2) = (4) < (3)

upon which follows—

(1) < (2) < (3) = (4)

and then—

(1) < (2) < (3) < (4)

and again—

(1) < (2) < (3) < (4)

but notwithstanding that the two groups, (2) and (4), are of equal mass in methyldiacetylglycerate, and the two groups, (3) and (4), in ethyldiacetylglycerate, yet neither of these compounds even approaches inactivity, nor is there any change of sign or direction in the activity exhibited by this series of compounds.

It is evident, therefore, that this more recent extension of the theory of the asymmetric carbon-atom has not yet been so formulated as to fully explain all the known facts. This further development of the theory is, in fact, in that most interesting phase of its evolution, when each new investigation bearing on it is eagerly awaited, to see in how far it will support and strengthen the hypothesis, and in what it will require its change and correction. This is indeed the great value of theoretical speculation, that it stimulates investigations and researches which would otherwise have possibly never been made at all, and in this way leads to the earlier and more rapid discovery of all that is true, lasting, and irrefragable.

ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN of Leipzic.

(Concluded from p. 34).

The New Plate Sensitive to the Ultra-Violet Rays.

A PLATE coated with pure silver bromide would in any case be most serviceable for photographing the rays of the smallest wave-length. For a long time I thought of using the Daguerreotype plate, which seemed for this purpose better adapted than the gelatin plate, as being free from retarding absorbents, if sensitised according to the process which Edmund Becquerel used for taking the solar spectrum. That I desisted from its use was due to its moderate sensitiveness and the manner of its formation.

Attempts to cover plates with an emulsion of silver bromide poor in gelatin proved entirely unsuccessful. The silver bromide deposited on the plate prior to the congelation of the coating, and there was formed above it a stratum of gelatin almost free from silver bromide, which prevented any result of the most refrangible rays. But when I exposed to the spectrum pure silver bromide spread out upon a plate of mirror-glass, I obtained a basis for the preparation of a plate such as I required for my experiments.

Pure silver bromide gave a very intense image of the spectral region beyond 185·2 $\mu\mu$, many times denser than any of the gelatin plates hitherto exposed. Here, then, was attained, for the first time—even if in a very imperfect degree—what had hitherto been wanting in all my proofs: the intensity required for a clear image of the lines. This proof, on pure silver bromide, imperfect as it might be, acquired in the sequel a fundamental importance for my work; it formed the initial point of a photochemical investigation—not yet complete—on the behaviour of the silver haloids of gelatin and its constituents soluble in water, of collodion, gum arabic, and agar-agar in ultra-violet light.

Among the principal results of this investigation ranks a new photographic plate of great sensitiveness for the ultra-violet rays and of corresponding intensity. With this, the above-named fluor-spar train, and with exclusion of air, I have subsequently obtained proofs of the extreme ultra-violet of faultless sharpness. From here date my better results with the more strongly deflected rays.

For two and a half years I have photographed all rays the wave-length of which is below 185 $\mu\mu$ exclusively with this plate, which is for the present the only means which allows of the observation of this region of the spectrum.

The new plate develops its maximum sensitiveness in the most refrangible ultra-violet. For instance, in the spectrum of aluminium it always shows first the line 32, and afterwards the other lines. Towards the red its sensitiveness decreases gradually, and from the cyanogen blue very rapidly, so that in the green it becomes coloured only on very energetic insolation. Hence for the less refracted ultra-violet, and for the visible spectrum, it is less susceptible than for the remainder of the spectrum.

This smaller sensitiveness renders it all the more suitable for the photography of all the more strongly de-

* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

flected violet rays. For as against the diffused light derived from the interior of the prism and of the lenses of the apparatus—which in gelatin plates is so apt to veil the back-ground, and obscures all the more tender effects of the light—it is so little sensitive that it bears exposure for hours without danger of veiling. It presents, therefore, besides the desired sensitiveness, the advantage which was previously to be obtained only from a suitable filter for the rays.

The treatment of the new plate does not differ from that of the gelatin plate. The development is effected with pyrogallic acid and soda and is generally completed in two minutes. The fixing-bath is a solution of hyposulphite of soda in water (1 : 4). The fixation is very rapid; a few seconds being generally sufficient. The fixing-agent can be washed out in a minute, and the drying does not last much longer.

The microscopic examination of the plate can always be undertaken in a few minutes after the development is completed. This is an advantage probably not possessed by any other plate in an equal extent.

The negative, as to its intensity and its grain, depends on the preparation of the plate. It may have a very fine grain, but it is then never so intense as with a coarser grain, where it quickly attains absolute opacity. Indeed, plates which otherwise give a finely granular image can be brought to the utmost intensity, but not without a simultaneous increase of the size of the grain when the plate becomes less brilliant.

For microscopic measurements, for the comparator, the intense—*i.e.*, coarsely granular—image is far more suitable than the finely granular. This fact does not harmonise with previous observations made on other plates, according to which the finely granular image shows the better defined lines.

The image of the new plate can readily be magnified one hundred times without being rendered useless for measurements.

Distortions of the negative image, such as may readily occur with gelatin plates, are, in my opinion, here quite excluded.

The production of the new plate presents as yet difficulties. I have therefore turned my attention entirely to improving the method of preparation, which goes hand in hand with the development of the photography of the new rays.

The process which I now make use of I do not consider trustworthy for publication. I also wish to give at the same time a series of normal accessory facts in their regular connection. To this end the verification of some of these results is necessary. Hence I prefer to treat the photochemical part of this investigation separately, and to defer publication until its definite conclusion.

GENERAL METHOD FOR THE VOLUMETRIC DETERMINATION OF SILVER IN ANY STATE WHATEVER.

By G. DENIGÈS.

THE ordinary volumetric determination of silver founded on the use of an alkaline chloride as reagent and potassium chromate as indicator requires us to operate in a medium strictly neutral; it is further affected by the presence of a considerable number of organic compounds, and is restricted to salts of silver soluble in water. The method of Volhard-Charpentier with potassium sulphocyanide is more general, since it permits us to operate in presence of nitric acid, but it excludes all salts of silver insoluble in that medium. The method which we are about to describe extends, on the contrary, to all compounds of silver, without exception.

Liebig showed that on adding silver nitrate to potassium cyanide without excess of alkali there is formed a soluble double cyanide of silver and potassium according to the equation—

$$NO_3Ag + 2CyK = CyAgCyK + NO_3K,$$

and that an excess, even very slight, of the silver solution is shown by the precipitation of insoluble silver cyanide.

We have ascertained that this reaction, which does not take place well except in a chemically neutral liquid, and the final term of which is sometimes not easy to seize, is effected very easily in presence of free ammonia, and we may ascertain its completion by adding to the mixture, as an indicator, potassium iodide, which forms with a very slight excess of the silver salt, silver iodide, insoluble in ammonia, and producing a very distinct cloud.

Variations, even very considerable, in the proportion of ammonia added, the presence of potash or soda free or as carbonates, of chlorides, bromides, phosphates, &c., have no influence on the quantities of silver nitrate used, so that we have a very precise and convenient method for determining hydrocyanic acid, free or combined.

Inversely, the simultaneous use of ammonia and a standard solution of potassium cyanide permits the determination of any silver compound, whether soluble or insoluble in water—for all the compounds of silver are soluble in ammonia or in potassium cyanide, or may be rendered soluble by the previous use of nitric acid.

We must mention beforehand that the solutions of potassium cyanide used at the degree of dilution employed (1 per cent) are surprisingly stable, and, further, that this stability is increased by the presence of an excess of alkali.

It is thus that 20 c.c. of three solutions of pure CyK pure at 9 grms. per litre, one neutral, which I shall call A; a second, B, containing 25 c.c. of ammonia per litre; a third, C, containing 25 c.c. soap-boilers' lye (!), being added to 100 c.c. of water, 5 c.c. of ammonia, and a little potassium iodide absorbed on their transformation into double cyanide the quantities of decinormal silver nitrate stated below:—

	Solution A.	Solution B.	Solution C.
On preparation	13·85	13·85	13·85
After fifteen days	13·80	13·85	13·85
After boiling for one minute ..	13·40	13·80	13·85
" " three minutes	12·60	12·90	13·80
" " five "	11·90	12	13·75

This proves the invariability of standard of these solutions for the term of fifteen days and the great stability of the alkaline solutions in heat, especially those containing soda, the alkaline solutions being altered like neutral solutions when they had lost their ammonia.

This permanence of standard is very valuable as it meets the only objection which might be made to the method, and leads to the employment of alkaline solutions by preference.

The very varied and numerous determinations of compounds of silver mentioned below were effected with samples of great purity.

About $\frac{1}{100}$th part of the equivalent of the substance, chlorate, chloride, bromate, bromide, iodate, sulphate, acetate, &c., was dissolved in 10 c.c. of ammonia and 5 c.c. of water, cold or gently heated; for the ferrocyanide, the bromide, and especially the iodide, a standard solution of CyK—of about 1 per cent—is added at the same time, which for the other salts is added only after solution.

For the phosphates, chromates, oxides, and especially for the sulphide, it is preferable to dissolve the substance in a little nitric acid diluted with an equal volume of water, applying heat, then to supersaturate with ammonia and to add the CyK after it is cold.

The chromate often dissolves slowly in nitric acid, but if after heating for a few moments it still leaves a residue the addition of ammonia causes it entirely to disappear.

When the silver compound is completely dissolved, and is in presence of a small excess of ammonia (5 to 10 c.c.)

and 20 c.c. of the standard solution of CyK, we add 100 c.c. of water, a little potassium iodide, and add the decinormal solution of silver nitrate little by little until the permanent opacity appears.

The difference between the standard of the 20 c.c. of CyK used and the proportion of the silver solution consumed to obtain the final reaction corresponds to an equal quantity of the decinormal solution of the silver compound examined, whence it is easy to deduce the proportion by weight.

We have thus obtained, among other figures, all very satisfactory:—

Substance.	Weight taken. Grm.	Weight found. Grm.
ClAg	0·140	0·140
BrAg	0·155	0·154
IAg	0·221	0·219
PO_4Ag_3	0·111	0·109
$Cr_2O_7Ag_2$	0·216	0·216
SAg_2	0·155	0·153

As it might be expected, the iodide is the slowest to dissolve; it should be macerated for a long time in the cyanide in a stoppered flask by the aid of a gentle heat.

The advantage of the new method is found especially in its applications, which are numerous.

1. Volumetric determinations of precipitates of silver chloride.

2. Determination direct or by difference of soluble chlorides, especially in organic liquids.

3. Determination of xantho-uric compounds in urine.

4. Titration of potassium iodide by precipitation by silver nitrate in an ammoniacal solution.

5. Determination of all the substances, acetylenic carbides, hydrogen arsenide, and antimonide aldehyds, carbon monoxide (utilising Berthelot's ingenious reaction), capable of modifying the standard of silver salts in alcoholic, ammoniacal, or acid solutions.—*Comptes Rendus*, cxvii., p. 1078.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1893.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, January 10th, 1894.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from December 1st to December 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined all were found to be clear, bright, and well filtered.

During the month of December the changes in the chemical constituents of the Thames-supplied waters have been very slight. The decrease of temperature and the diminished amount of oxidation through the agency of plant growth have been followed by a minute but wholly unimportant increase in the organic carbon present, shown alike by the "combustion," the "oxidation," and the "colour tint." The increase, however, in each case is very small, the amount being, in fact, lower than it was in either of the months of December, January, February, or March last, although a trifle higher than in November. The following Table shows how favourably the month just ended compares with the corresponding month of last year:—

Comparison of the Averages of the Five Thames-derived Supplies for the Months of December, 1892 and 1893.

	Nitric acid.	Hardness, degrees.	Oxygen required per gallon.	Organic carbon per gallon.	Colour. Brown. : Blue.
	Means.	Means.	Means.	Means.	Means.
Dec., 1892.	1·054	17·70	0·060	0·134	28·8 : 20
,, 1893.	0·935	16·36	0·044	0·096	19·4 : 20

The singularly small rainfall which has characterised most of the months of the year 1893 has been continued to the end. The actual fall at Oxford during December was only 1·72 inch, whereas the mean rainfall for twenty-five years is 2·10 inches; the deficiency has therefore been 0·38 inch. With the exception of the months of February and July, when the fall was decidedly above the average, and October, when the mean fall was only just exceeded, every month has been conspicuously deficient in rain. The unusual character of the past year in this respect may, perhaps, be better appreciated if the rainfall is given in a tabular form, as set forth below:—

Table Showing the Rainfall in Inches at Oxford, Month by Month, During the Year 1893.

	Actual fall.	Mean of 25 years.	Deficiency.	Excess.
January	1·88	2·26	0·38	—
February	2·64	1·92	—	0·72
March	0·18	1·59	1·41	—
April	0·06	1·78	1·72	—
May	0·84	1·95	1·11	—
June	0·77	2·21	1·44	—
July	3·70	2·58	—	1·12
August	1·01	2·24	1·23	—
September . ..	0·57	2·66	2·09	—
October	2·65	2·56	—	0·09
November.. ..	1·68	2·31	0·63	—
December.. ..	1·72	2·10	0·38	—
	17·70	26·16	10·39	1·93

It is thus seen that there is a deficiency over the whole year of no less than 8·46 inches of rain, or nearly one-third of the mean quantity falling on that part of the gathering ground of the Thames valley supplying the chief sources of the river.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.

ON THE

DECOMPOSITION OF LIQUIDS BY CONTACT WITH POWDERED SILICA, &c.*

By Dr. G. GORE, F.R.S.

(Concluded from p. 33).

Influence of Nascent State.

IT is well known to chemical analysts that certain precipitates during their act of formation in particular liquids

* From the *Proceedings of the Birmingham Philosophical Society*, Vol. ix., Part I.

carry down with them by adhesion some of the soluble constituents of the liquids, and a very large amount of washing is required to remove the impurity.* In order, therefore, to test whether in such a case the precipitated powder during its freshly-formed or nascent state abstracted a larger portion of the dissolved substance than when in the usual previously-prepared condition, the following experiments were made:—Equivalent quantities of potassium sulphate and barium nitrate, sufficient to form 22·41 grains of potassium nitrate and 25·9 grains of barium sulphate, were dissolved in separate quantities of water to make in each case 12·5 c.m. of solution, and the latter solution was added to the former one in a stoppered bottle; at the same time 25·9 grains of barium sulphate were added to 25·0 c.m. of solution containing 22·41 grains of potassium nitrate in a second bottle. The two mixtures were then equally shaken and set aside to rest during thirty-six hours; the previously precipitated substance subsided in about one-fortieth the time of the other. To equal volumes of the clear decanted liquids were then added full equivalent quantities of sulphuric acid, and the mixtures evaporated to dryness and a constant weight of K_2SO_4. The liquid from the nascent sulphate gave a loss of 4·13 per cent, and that from the previously prepared sulphate, after correction for the volume occupied by the dry sulphate, gave a loss of 2·58 per cent = a difference of 1·55 between the two percentages. In a repetition of this experiment, the two liquids being analysed by means of protochloride of iron and potassium permanganate, the solution with the nascent powder again suffered the greatest loss of potassium nitrate, but the difference between the two percentages in this case was 1·21; the former analysis was the most reliable one.

According to the results of these experiments the amount of dissolved substance abstracted from the liquid is affected by the nascent state of the powder, and the nascent substance has greater effect than the previously prepared one.

Experiments with Titanic Acid.

This powder was finer than the silica; it was highly pure, but was not previously washed with the electrolytes.

Solution. No.	Per cent.	Grain.	Per cent.
141.	1·0 Na_2Co_3 lost	0·255 =	6·6
Analysed as in No. 76 after subsiding clear in four hours.			
142.	1·0 K_2CO_3 lost	0·23 =	5·95
Analysed as in No. 76 after subsiding clear in four hours.			
143.	1·0 KCy no effect		
Analysed as in No. 85 after subsiding clear in four hours.			
144.	0·1 Am. sesquicarb. lost	0·084 =	21·8
Analysed as in No. 76 after subsiding clear in sixteen hours.			
145.	1·0 Am. sesquicarb. lost	0·34 =	9·0
Analysed as in No. 76 after subsiding clear in sixteen hours.			
146.	1·0 AmHO lost	0·20 =	5·15
Analysed as in No. 76. Required forty hours to perfectly subside.			

The titanic acid had usually a much smaller effect than the silica.

Experiments with Stannic Oxide.

147. The oxide was very pure and a finer powder than the silica; it was not previously washed with the electrolytes. The 1 per cent solutions of sodium carbonate, potassium carbonate, potassium cyanide, ammonium sesquicarbonate, and caustic ammonia were analysed after a period of four hours, but neither of them showed any abstraction either of the salt or of the water by the oxide. The action of this oxide was feebler than that of any other of the powders examined.

Experiments with Alumina.

The alumina was the precipitated pure substance, and was treated in a similar manner to the silica. It was previously heated to redness and perfectly washed with water.

Solution. No.	Per cent.	Grain.	Per cent.
148.	0·02 Iodine lost	0·0116 =	15·0
Analysed as in No. 140 after standing sixteen hours.			
149.	1·0 AmCl lost	0·125 =	3·3
Analysed as in No. 1 after standing sixteen hours.			
150.	10·0 AmCl lost	0·76 =	2·0
Analysed as in No. 1 after standing sixteen hours.			
151.	1·0 AmBr lost	0·12 =	3·10
Analysed as in No. 1 after standing sixteen hours.			
152.	10·0 AmBr no effect		
Analysed as in No. 1 after standing sixteen hours.			
153.	0·1 Am. sesquicarb. lost	0·116 =	30·0
Analysed as in No. 76 after standing sixteen hours.			
154.	1·0 Am. sesquicarb. lost	1·01 =	26·1
Analysed as in No. 76 after standing sixteen hours.			
155.	10·0 Am_2SO_4 lost	0·378 =	0·98
Analysed as in No. 44 after standing sixteen hours.			
156.	1·0 AmHO lost	0·505 =	13·1
Analysed as in No. 76 after standing sixteen hours.			
157.	10·0 AmHO no effect		
Analysed as in No. 76 after standing sixteen hours. With 200 grains of the powder there was also no effect.			

The effects with alumina were generally less than those with silica.

Experiments with Ferric Oxide.

The oxide was very pure, but was not previously washed with the electrolytes; it subsided quickly.

Solution. No.	Per cent.	Grain.	Per cent.
158	1·0 Na_2CO_3 no effect		
Analysed as in No. 76 after standing sixteen hours.			
159.	1·0 K_2CO_3 lost	0·131 =	3·4
Analysed as in No. 76 after standing sixteen hours.			
160.	1·0 KCy no effect		
Analysed as in No. 85 after standing sixteen hours.			
161.	1·0 Am. sesquicarb. lost	0·174 =	4·5
Analysed as in No. 76 after standing sixteen hours.			
162.	1·0 AmHO no effect		
Analysed as in No. 76 after standing sixteen hours.			

The effects were usually feebler than those obtained with alumina or silica.

Experiments with Magnesium Carbonate.

Corrections were made for the solubility of the carbonate in water.

Solution. No.	Per cent.	Grain.	Per cent.
163.	1·0 Na_2CO_3 lost	0·336 =	8·7
Analysed as in No. 76 after standing sixteen hours.			
164.	1·0 K_2CO_3 lost	0·51 =	13·2
Analysed as in No. 76 after standing four hours.			
165.	1·0 KCy no effect		
Analysed as in No. 85 after standing sixteen hours.			
166.	1·0 Am. sesquicarb. lost	0·178 =	4·6
Analysed as in No. 76 after standing sixteen hours.			
167.	1·0 AmHO lost	0·203 =	5·26
Analysed as in No. 76 after standing four hours.			

The effects were much more feeble than those obtained with silica.

* In making alumina from ammonia alum and aqueous ammonia, sulphate of ammonia adhered to the precipitated alumina, even after apparently perfect washing, and was found after subsequently heating the precipitate to bright redness.

Experiments with Calcium Carbonate.

168. With the usual weights of the pure precipitated carbonate, and the usual volumes of 1 per cent solutions of the carbonates of sodium, potassium, and ammonium, potassium cyanide, and caustic ammonia, no alteration of strength of either of the liquids occurred.

Experiments with Barium Sulphate.

Solution. No.	Per cent.	Grain.	Per cent.
169.	1·0 HCl no effect		
	Analysed as in No. 1 after standing sixteen hours.		
170.	1·0 NaCl gained	0·08	= 2·07
	Analysed as in No. 1 after standing sixteen hours.		
171.	0·5 K_2CO_3 loss of	0·098	= 5·10
	Analysed as in No. 76 after standing sixteen hours.		
172.	1·0 K_2CO_3 gained	0·138	= 3·59
	Analysed as in No. 76 after standing sixteen hours.		
173.	10·0 K_2CO_3 no effect		
	Analysed as in No. 76 after standing sixteen hours.		
174.	1·0 KCy no effect		
	Analysed as in No. 85 after standing sixteen hours.		

The effects were feeble in comparison with those obtained with silica.

Experiments with Mixtures of Powders.

175—176. A mixture of 25 grains of silica and 25 grains of alumina previously washed with a solution of ammonium chloride, then with water, and ignited, was shaken with 25·0 centims. of a 10·0 per cent solution containing 38·7 grains of sal ammoniac. No change of composition of the liquid occurred (compare Nos. 125 and 150). A similar mixture of 25 grains each of silica and sulphate of barium, previously treated with a solution of potassium carbonate, washed and ignited, was employed with 25 c.c. of a 1·0 per cent solution of the carbonate; the solution lost 0·73 grain of K_2CO_3 = 19·7 per cent (compare Nos. 111 and 172). Mixed powders, like mixed solutions, appear to disturb each other's effect.

General Remarks and Conclusions.

The results of this research show clearly that the power of abstracting dissolved substances from liquids is a common property of finely-divided solid bodies, and that the amount abstracted varies with the following circumstances:—(1) The kind of powder employed; (2) the degree of fineness of the powder, and consequently the amount of its surface; (3) the kind of dissolved substance; (4) the proportion of powder to dissolved substance; (5) the kind of solvent; (6) the proportion of solvent to powder; (7) the proportion of dissolved substance to solvent; and (8) in a small degree with the temperature. The union takes place quickly, and a longer period of time has but little influence. Finely precipitated silica possesses the property in the greatest degree, and alkaline substances are the most affected.

The fact that the amount of effect varied with the *kind* of powder, and was usually greater with silica than with other substances of equal or even greater degree of fineness, proves that it is not entirely due to increased amount of surface of the liquid in contact with the solid. The action of the powder is not limited to the dissolved substance, but extends also to the solvent; this is proved by the circumstance that in some cases there is a *gain* of dissolved substance by the external mass of the liquid, indicating an abstraction of the *solvent* by the powder. The results clearly show that the action depends both upon the solid and upon the liquid; in this respect it is similar to chemical union.

The action is evidently limited to the superficial layers of molecules of the solid and liquid; the finer the powder and the larger the proportion of it to the liquid the greater usually was the effect. The phenomenon is also an instance of molecular balance in which the equilibrium is disturbed by altering either the nature or the amount of either of the substances present. It is like that of mixing an equivalent of soda solution with an equivalent each of nitric and sulphuric acids, in which case the base divides itself between the two acids in a proportion which varies with the amount of each of the substances present; in a similar manner the dissolved substance divides itself between the powder and the solvent, and the powder divides itself between the solvent and the dissolved substance.

The action is a reversible one:—By shaking an insoluble powder with a solution of a salt or acid the former usually abstracts the salt or acid from the solvent; whilst by subsequently shaking the drained powder with the solvent the latter removes the salt or acid from the powder. These apparently contradictory effects are very similar to those obtained by passing hydrogen over red-hot oxide of iron, and then passing the resulting steam over the red-hot reduced iron; the chief difference in the two cases being that in the former case the changes are physical and feeble, whilst in the latter they are chemical and strong. The circumstance which determines the reversal is probably a change in come of the molecular velocities of the substances present.

Bearing upon the same subject, Pouillet, and subsequently Regnault and Meissner, have shown that when an insoluble non-corroded powder absorbs a liquid a minute amount of heat is evolved (*Annales de Chemie*, 1822, vol. xx., pp. 141—162; "Gmelin's Handbook of Chemistry," vol. i., p. 300; *Nature*, Nov. 4, 1886, p. 24); and I have recently made many experiments of a similar kind, with a different class of liquids, and obtained the same general effect. As I found that heat was evolved in nearly every case, the powder probably abstracts some of the dissolved substance, the water, or both, in all cases. In this respect also, *i.e.*, the evolution of heat, the present phenomena are similar to those of chemical union.

As the portion of liquid in the pores of the powder has a somewhat different composition from the remainder of the bulk, it must also have somewhat different properties; and as the action is attended by evolution of heat, the abstracted portion of liquid has probably less energy and greater specific gravity usually than the remainder. Rücker has found that the thinner parts of a soap film have different electric conduction resistance than the thicker ones (*Nature*, June 1, 1893, p. 116).

As the action appears to be in several fundamental respects the same as that occurring in well-known cases of chemical change and equilibrium, although more feeble and more simple, it is probably determined by the same general laws and conditions, and capable of the same fundamental explanation.

A mechanical explanation I venture to offer of the phenomenon is that the molecules of the powder and of the liquid, being brought into mutual contact, a small proportion of the molecular motion of the former substance is neutralised by an equivalent proportion of that of the latter, and converted into heat, and the two sets of molecules being thus brought into nearer proximity, and having lost a portion of their motion, retain their new positions and distances. I have not ascertained by experiment whether a contraction of volume of the liquid really occurs during the action.

Although the substances do not appear to unite together in chemical equivalent proportions, the third law of motion requires that the action and reaction of the two sets of molecules must be equal, and that the phenomena must in some form include equivalent quantities of the substances and of neutralised energy. Equal weights of silica of the same degree of fineness and amount of active surface ought to abstract equivalent quantities of acid + water, salt + water, &c., the water or other solvent forming a part of the equivalent weight; all that adheres to 100 parts of silica in one case ought to be mechanically equivalent to all that adheres to it in another case.

The results appear to throw some light upon the purification of water by filtration through the earth and upon

agriculture, and to show that the alkaline constituents of soils are retained much more by the silica than by the alumina. The effects of silica upon weak solutions of potassium cyanide indicate that the great loss of the latter substance in the commercial process of extracting gold and silver from powdered quartz is largely due to the "adhesion" of that salt to the silica. And the results obtained with silica and a very weak solution of iodine indicate a possible method of extracting the latter substance from solutions, and the recovery of the iodine from the silica by distillation. Additional experiments with other kinds of powder and liquids would probably yield other practical results. The research is evidently capable of further extension by the use of a greater variety and number of substances, and by the employment of mathematical methods. The general result of the research is to more closely connect together the subjects of physics and chemistry.

Additional Experiments and Remarks.

Solution No.	Grs.		C.m.	Per cent solution.		Grain.	Per cent.
177.	100	Al_2O_3 + 25 of	10	NaCl lost		0·42	= 1·10
		Analysed as in No. 1.					
178.	50	Al_2O_3 + 25 of	10	$CdSO_4$	„	0·275	= 0·71
		Analysed as in No. 30.					

In a repetition of experiment 178, employing the same weight (viz., 38·75 grains of the salt), and similar in every respect except that the alumina was simply allowed to fall in gradually and subside, without being at all shaken, exactly the same numerical results were obtained.

179—180. A first treatment of 180 c.m. of a 10 per cent solution of the potassium cyanide with 360 grains of the precipitated silica, removed 7·14 grains, or 2·56 per cent of the salt. And a second treatment of 45 c.m. of the clear residuary liquid, with 90 grains of the silica, removed a further amount of 1·92 grains, or 2·69 per cent more of the residuary cyanide. These results indicate that the degree of adhesion to the silica of the salt in the residuary solution was not widely different from that in the original liquid, and that the molecules of the former solution were not less active than those of the latter.

Although in all cases the wetting of the powder and the abstraction effect appeared to be complete immediately after the thorough shaking of the mixture, a very slight evolution of minute air-bubbles, and consequently a small extension of amount of contact surface of the liquid and solid, and the substitution of the liquid film for the air one, continued, with peroxide of iron the escape of air-bubbles ceased in about half an hour, but with silica and alumina it continued during several days. With coarse sand the air-bubbles did not at all appear.

The action occurring in all the experiments of this research is analogous to that of chemical substitution; the liquid displaces a film of air, and the powder displaces portions of the solvent and the dissolved substance from their union with each other, and unites with them instead; but being only a feeble action it does not overcome strong chemical union.

It is not improbable that the phenomenon of adhesion of solvents and dissolved substances to powders is related to that of increased strength imparted to canvas by wetting it with water (*Journ. Soc. Chem. Industry*, October 31, 1893, vol. xii., p. 825), and to the well-known facts that powders contract, and dry ropes become shorter when wetted.

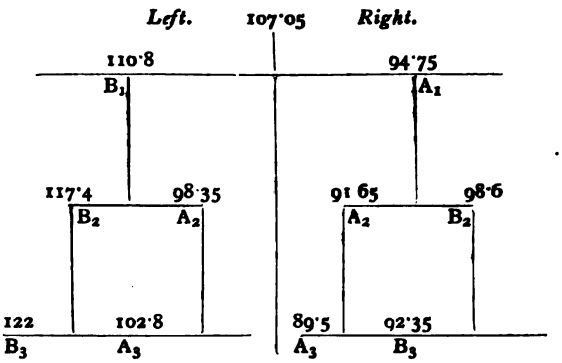
Carbon Dioxide as a Germicide.—Researches recently conducted by Dr. Hankin in the Government Laboratory at Agra have led to the satisfactory result that the carbonic acid in aërated waters is destructive to pathogenic micro-organisms. The microbe of cholera perishes in a few hours after bottling. The bacillus of typhoid is more persistent, but it also is destroyed within a week or ten days.

NOTES ON THE OXIDES CONTAINED IN CERITE, SAMARSKITE, GADOLINITE, AND FERGUSONITE.*

By WOLCOTT GIBBS, M.D.,
Rumford Professor (Emeritus) in Harvard University.

(Continued from p. 18.)

THE following diagram enables us to take in all the results at a glance:—



It must be noted that in the above and on the diagram, B_1, B_2, B_3, &c., denote basic or oxychlorides: A_1, A_2, A_3, &c., neutral or relatively acid chlorides. The analyses were not pursued further because the material taken was exhausted by the separations accomplished. The examination of the results obtained in this particular case by the basic-chloride process leads to interesting conclusions. In the first place, it will be remarked that the atomic masses of the insoluble basic chlorides increase with each successive separation into basic and acid chlorides, while the neutral or relatively acid chlorides give diminishing atomic masses. In the cases of these last, three successive operations give a nearly pure yttria, with atomic mass 89·5. The rate of increase of the atomic masses of the successive portions B_1, B_2, B_3, is about 5·3 units for each operation. The rate of decrease of the portions A_1, A_2, A_3, is about 2·6 units for each operation. It is not to be expected that perfectly uniform results will be obtained even when the process is applied to the same mixture of oxides, because the amount of separation into basic and acid chlorides by each operation must depend very much upon the temperature of the muffle and the length of time during which the heat is applied. In the second place, it must be noted that, while a very nearly pure yttria is obtained in three operations, this does not represent the whole quantity of the earth in the compound. It will also be seen that a decided advantage must be secured by making mixtures of the products having nearly the same atomic masses, and then applying the method of separation to these.

Other applications of the method give, as I will now show, substantially similar results. The next substance examined was a mixture of oxides received from Dr. Shapleigh, and obtained from residual mother-liquors of cerite and monazite salts. The oxide was dissolved in chlorhydric acid, and purified by a current of sulphydric acid. Of the mixed oxalates,—

(69).	0·5622 grm.	gave	0·1715 grm.	C_2O_3 = 30·50	per cent.
(70).	0·4782	„	0·1458	C_2O_3 = 30·50	„
(71).	0·4355	„	0·1326	C_2O_3 = 30·47	„
(72).	0·6100	„	0·2778	R_2O_3 = 45·55	„
(73).	0·6904	„	0·3141	R_2O_3 = 45·50	„

Atomic mass 137·25.

I also determined the mean atomic mass after separating the cerite earths by means of sodic sulphate in the usual manner. Of course some yttria went down with the double sulphates.

* *American Chemical Journal*, xv., No. 7.

(74). 0·2440 grm. gave 0·0946 grm. C_2O_3=38·77 per cent.
(75). 0·2438 ,, 0·0946 ,, C_2O_3=38·80 ,,
(76). 0·4597 ,, 0·2146 ,, R_2O_3=46·68 ,,
(77). 0·3570 ,, 0·1668 ,, R_2O_3=46·72 ,,
Atomic mass 106·05.

The oxides with atomic mass 106·05 were then treated by the oxychloride process.

Portion B_1 Left.
(78). 0·4027 grm. gave 0·1505 grm. C_2O_3=37·38 per cent.
(79). 0·5204 ,, 0·1943 ,, C_2O_3=37·35 ,,
(80). 0·6947 ,, 0·3250 ,, R_2O_3=46·78 ,,
(81). 0·9233 ,, 0·4323 ,, R_2O_3=46·82 ,,
Atomic mass 111·3.

Portion B_2 Left.
(82). 0·4127 grm. gave 0·1464 grm. C_2O_3=35·49 per cent.
(83). 0·3215 ,, 0·1142 ,, C_2O_3=35·51 ,,
(84). 0·5885 ,, 0·2668 ,, R_2O_3=45·33 ,,
(85). 0·6205 ,, 0·2814 ,, R_2O_3=45·35 ,,
Atomic mass 113·95.

Portion A_1 Right.
(86). 0·4332 grm. gave 0·1630 grm. C_2O_3=37·63 per cent.
(87). 0·3239 ,, 0·1217 ,, C_2O_3=37·57 ,,
(88). 0·6813 ,, 0·3062 ,, R_2O_3=44·94 ,,
(89). 0·6749 ,, 0·3035 ,, R_2O_3=44·95 ,,
Atomic mass 105·1.

Portion A_2 Right.
(90). 0·3317 grm. gave 0·1161 grm. C_2O_3=35·02 per cent.
(91). 0·3216 ,, 0·1126 ,, C_2O_3=35·00 ,,
(92). 0·6800 ,, 0·2823 ,, R_2O_3=41·52 ,,
(93). 0·6529 ,, 0·2709 ,, R_2O_3=41·50 ,,
Atomic mass 104·05.

B_2 Right.
(94). 0·3785 grm. gave 0·1314 grm. C_2O_3=34·73 per cent.
(95). 0·2882 ,, 0·0999 ,, C_2O_3=34·68 ,,
(96). 0·6187 ,, 0·2676 ,, R_2O_3=43·25 ,,
(97). 0·6421 ,, 0·2770 ,, R_2O_3=43·24 ,,
Atomic mass 110·45.

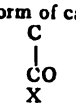
A_2 Left.
(98). 0·3458 grm. gave 0·1290 grm. C_2O_3=37·31 per cent.
(99). 0·4089 ,, 0·1523 ,, C_2O_3=37·24 ,,
(100). 0·6892 ,, 0·3062 ,, R_2O_3=44·43 ,,
(101). 0·5986 ,, 0·2660 ,, R_2O_3=44·44 ,,
Atomic mass 104·75.

A_3 Right.
(102). 0·3002 grm. gave 0·1162 grm. C_2O_3=38·73 per cent.
(103). 0·3251 ,, 0·1260 ,, C_2O_3=38·77 ,,
(104). 0·6667 ,, 0·3031 ,, R_2O_3=45·44 ,,
(105). 0·7642 ,, 0·3478 ,, R_2O_3=45·51 ,,
Atomic mass 102·75.

(106). B_3 Right.
(107). 0·3426 grm. gave 0·1307 grm. C_2O_3=38·16 per cent.
(108). 0·3401 ,, 0·1298 ,, C_2O_3=38·18 ,,
(109). 0·8197 ,, 0·3728 ,, R_2O_3=45·46 ,,
(110). 0·7623 ,, 0·3467 ,, R_2O_3=45·47 ,,
Atomic mass 104·65.

(To be continued.)

Study on Eserine. — A. Petit and Polonovsky. — Eserine, $C_{15}H_{21}N_3O_2$, is a ternary mon-acid base. Of the three atoms of nitrogen which it contains one only gives its basic character. One of the nitrogens of eserine is connected to a group, CH_3. This substituted nitrogen does not happen to be the same as that which fixes the elements of the alcoholic iodide. Eserine contains an atom of oxygen in the form of carbonyl, probably—



The second atom of oxygen seems to be belong to a phenolic grouping.—*Bull. de la Soc. Chim. de Paris*, ix.-x., No. 24.

ON THE

CUPRIAMMONIUM DOUBLE SALTS.*

By THEODORE WILLIAM RICHARDS and HUBERT GROVER SHAW.

(Concluded from p. 28.)

4. *Cupriammonium Formibromide*, $Cu(NH_3)_2BrCHO_2$.

CUPRIAMMONIUM formibromide is made after a method essentially similar to that employed in making the corresponding compound of acetic acid. The salt is more difficult to obtain in a pure state: but any reasonably concentrated solution containing bromine, copper, much formic acid, and ammonia in very slight excess, will deposit the deep "robin's egg" blue crystals of the desired salt upon the addition of alcohol. The possibility of the formation of basic salts of copper is diminished if the excess of ammonia is added after the addition of the alcohol. The salt possesses no unexpected properties, except that the colour of the short needles is much less brilliant and crude than that of cupriammonium acetobromide.

A similar compound containing chlorine instead of bromine has been prepared, and analysed with results which were sufficiently accurate to show the identity of the compound: but it was thought desirable to study more carefully the conditions necessary for its preparation in a pure state before publishing the results. Moreover, a more complex formibromide of most interesting aspect and composition has been made. This substance also awaits further study.

Analyses of Cupriammonium Formibromide.

I.—0·2192 gr. of the substance gave on electrolysis 0·0621 gr. of copper.
II.—0·2164 gr. of the substance yielded on electrolysis 0·0618 gr. of copper.
III.—0·1386 gr. of the substance yielded a distillate of ammonia which required for neutralisation 12·32 c.c. of decinormal acid.
IV.—Similarly, 0·1180 gr. of the substance required 10·46 c.c. of decinormal acid.
V.—0·1599 gr. of the substance gave 0·1371 gr. of argentic bromide.
VI.—0·2414 gr. of the substance gave 0·2063 gr. of argentic bromide.
VII.—0·1678 gr. of the substance gave 0·1429 gr. of argentic bromide.
VIII.—0·2062 gr. of the substance yielded on combustion 0·0403 gr. of carbon dioxide.
IX.—0·2435 gr. of the substance yielded on combustion 0·0469 gr. of carbon dioxide.

No.	Copper.	Ammonia.	Bromine.	Formic acid, CHO_2.
I.	28·30			
II.	28·56			
III.		15·17		
IV.		15·13		
V.			36·49	
VI.			36·37	
VII.			36·24	
VIII.				19·93
IX.				19·70
Average	28·43	15·15	36·37	19·80

These analyses were made from several different samples (especially V., VI., and VII., which were all different), and hence they prove the definiteness of the compound. The averaged results are given below.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedin s of the American Academy of Arts and Sciences*.

	Calculated for $Cu(NH_3)_3BrCHO_2$.	Found.
Copper	28·56	28·43
Ammonia	15·33	15·15
Bromine..	35·90	36·37
CHO_2	20·21	19·80
	100·00	99·75

5. *Cupric Ammonic Acetochloride*, $CuCl_2.2NH_4C_2H_3O_2$.

Upon several occasions during the investigation just described, when concentrated solutions of approximately equivalent amounts of cupric chloride and ammonic acetate had been allowed to evaporate together, especially with addition of alcohol, bright green almost cubical crystals separated. These crystals were sometimes found to be mixed with small amounts of ammonic chloride, and sometimes almost pure. The substance is a double salt, and not a cupriammonium compound; hence it dissolves in water without apparent decomposition. The purest crystals gave the following analytical results.

Analyses of Cupric Ammonic Acetochloride.

I.—0·3132 gr. of the substance gave 0·0689 gr. of copper.

II.—0·2649 gr. of the substance gave 0·0585 gr. of copper.

III.—0·1180 gr. of the substance gave 0·1181 gr. of argentic chloride.

IV.—0·2091 gr. of the substance gave 0·2150 gr. of argentic chloride.

V.—0·2121 gr. of the substance yielded enough ammonia to require 14·47 c.c. of decinormal acid.

VI.—0·2158 gr. of the substance required 14·20 c.c. of acid.

VII.—0·1930 gr. of the substance required 13·83 c.c. of acid.

VIII.—0·2648 gr. of the substance gave 0·1633 gr. of carbon dioxide.

No.	Copper.	Chlorine.	Ammonium.	$C_2H_3O_2$.
I.	22·00			
II.	22·09			
III.		24·75		
IV.		25·35		
V.			12·34	
VI.			11·88 (?)	
VII.			12·98	
VIII.				41·35
Average	22·05	25·05	12·40	41·35

	Calculated for $Cu(NH_4)_2Cl_2(C_2H_3O_2)_2$.	Found.
Copper	22·03	22·05
Chlorine	24·56	25·05
Ammonium	12·52	12·40
Acetic acid	40 89	41·35
	100·00	100·85

6. *Tetrammon-Tricupriammonium Bromide*, $3Cu(NH_3)_2Br_2.4NH_3$.

Long ago Rammelsberg (*Pogg. Annalen*, lv., 246) described two compounds of ammonia and cupric bromide, to one of which, consisting of dark green crystals, he ascribed the formula $CuBr_2.3NH_3$, and to the other, consisting of a bright blue powder, he ascribed the formula $CuBr_2.5NH_3$. Recent investigation (T. W. Richards, *Ber. d. Chem. Ges.*, 1890, p. 3790) has shown that the latter of the two substances must have been in reality $CuBr_2.6NH_3$, which had lost some of its very loosely combined ammonia by exposure to the air. The same investigation brought to light an olive-green substance having the formula $Cu(NH_3)_2Br_2$.

Repeated attempts were made at the same time to obtain Rammelsberg's first substance. The product of these trials invariably consisted of deep indigo, almost black crystals, which contained noticeably more ammonia than the amount required by Rammelsberg's formula. These deep blue crystals are best obtained by adding very cautiously strong hydrobromic acid to a mixture of cupric bromide, alcohol, and just enough aqua ammonia to keep all the copper in solution. Upon the addition of enough acid to neutralise the ammonia, the crystals—which are almost insoluble in alcohol—begin to form.

Upon exposure to the air in a moist state these crystals lose ammonia rather rapidly; but when dry they are much more stable. Gentle heat (160°) readily converts them completely into the olive-green $Cu(NH_3)_2Br_2$, which still retains the crystalline form of the more complex salt. It is not impossible that Rammelsberg's green crystals consisted originally of the indigo-coloured substance, which had lost superficially a little of its ammonia.

Tetramnon-tricupriammonium bromide is decomposed by water, a noticeable amount of copper going into solution in the form of a soluble compound containing proportionally more ammonia than the original substance. The reaction which takes place may possibly be represented somewhat as follows:—

$$Cu_3(NH_3)_{10}Br_6 + 4H_2O = [Cu(NH_3)_6Br_2 + 4NH_4Br + Aq] + 2Cu(OH)_2.$$

The amount of water present undoubtedly determines to a large extent the exact nature of the cupriammonium compound which remains undecomposed.

A great number of analyses of the indigo salt were made; partly because of the unusual nature of the formula which they indicated, and partly because the crystals, constantly appearing under many varying conditions in the work which has just been described, needed identification.

Analyses of $Cu_3(NH_3)_{10}Br_6$.

I.—0·4730 gr. of the substance yielded 0·1075 gr. of copper.

II.—0·4540 gr. of the substance yielded 0·1033 gr. of copper.

III.—0·2614 gr. of the substance yielded 0·0594 gr. of copper.

IV.—0·4269 gr. of the substance yielded 0·5721 gr. of argentic bromide.

V.—0·4084 gr. of the substance yielded 0·5476 gr. of argentic bromide.

VI.—0·2884 gr. of the substance yielded 0·3861 gr. of argentic bromide.

VII.—0·1776 gr. of the substance yielded an amount of ammonia requiring 20·67 c.c. of decinormal acid for neutralisation.

VIII.—0·1245 gr. of the substance required 14·77 c.c. of the same acid.

IX.—0·1099 gr. of the substance required 12·71 c.c. of the same acid.

X.—0·1288 gr. of the substance required 15·20 c.c. of the same acid.

XI.—0·1175 gr. of the substance required 13·85 c.c. of the same acid.

No.	Copper.	Bromine.	Ammonia.
I.	22·73		
II.	22·75		
III.	22·72		
IV.		57·03	
V.		57·06	
VI.		56·97	
VII.			19·86
VIII.			20·25
IX.			19·74
X.			20·14
XI.			20·19
Average ..	22·73	57·02	20·06

Result.

	Calculated for $CuBr_3NH_3$.	Calculated for $(CuBr_3)_3(NH_3)_{10}$.	Found.
Copper	23·15	22·68	22·73
Bromine	58·21	57·03	57·02
Ammonia ..	18·64	20·29	20·06
	100·00	100·00	99·81

It is evident that this paper is merely an introduction to the possibilities in the direction indicated. Not only have other compounds of the same acids been already discovered, but many other acids, notably hydriodic, lactic, sulphocyanic, &c., show that they are capable of forming similar compounds. Moreover, the substituted ammonias may apparently take the place of the simple substance in most of the compounds. A few of these preparations are to be seen in the University exhibit at the World's Columbian Exhibition. The study of all these interesting substances will be continued in the immediate future at this Laboratory.

NOTICES OF BOOKS.

Le Cuivre. By PAUL WEISS. Paris: J. Baillière and Sons.

THE volume now before us is the outcome of a series of visits, by the author, to all the principal copper mines and works in Europe. M. Weiss claims that it is not merely a technical work for the use of manufacturers, but that it will also be found very useful to engineers and others who wish to keep themselves *au courant* with the latest developments of the copper industry.

The book is divided principally into three parts:—Part I. deals with the origin and occurrence of copper, its properties and its alloys, and gives an interesting series of figures, reproduced from photographs taken by M. Guillemin, showing the molecular structure of various samples of copper, unrefined and refined, as well as that of some of its principal alloys.

In Part II. we find a full description of the metallurgy and production of copper, both by the dry and wet methods, a very interesting chapter being devoted to its electro-deposition.

The third and last part deals with the applications of copper in various industries, and considers it from the commercial point of view; a valuable table and diagram are given, showing the rise and fall in the value of copper from the year 1876 to the year 1889, the most remarkable feature being the quick rise to £100 per ton and the sudden collapse to about £40 per ton, owing to the operations of the well-known copper ring.

The book is plentifully illustrated by ninety-six figures and plates, and the letterpress leaves nothing to be desired.

Do you Know it? If not you Should. By C. E. CLARK. London: Saxon and Co.

THE number of encyclopedias, already very large, is further increased by the publication of this curiously-named volume. Although only of the "pocket-book" size and modest in its pretensions, as set forth by the author in the "Forewords" (as he quaintly calls the preface), it still contains a considerable amount of interesting information, dealing almost entirely with legal and political matters. The frequently used, but imperfectly understood terms, so affected by modern newspaper writers, are explained, and in most cases their origin is given.

We must, however, take exception to some of the so-called "mispronounced" names on page 139, the pronunciation given in several cases being different to that in use by personal friends bearing the names.

In conclusion, the print is clear and the index good, though no plan seems to have been adopted with regard to the classification of subjects.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 2, January 8, 1894.

At the meeting of the Academy M. Marey was elected Vice-President for the year by 29 votes as against 26 recorded for M. Chatin. MM. Fizeau and Daubrée were elected Members of the Central Administrative Commission for the current year.

Studies on the Formation of Carbonic Acid and the Absorption of Oxygen by Leaves Detached from Plants. Purely Chemical Reactions.—MM. Berthelot and G. André.—The proportions of oxygen would become much more considerable if we regarded the totality of the carbonic acid capable of being evolved in the midst of the hydrogen at the end of a time more or less long. Our calculation furnishes minimum numbers for the oxygen absorbed without compensation. Doubtless it is not possible to isolate strictly these different effects. Still our figures give at least an idea of their respective functions in the purely chemical metamorphoses of the leaf. It is indispensable to take account of this in the study of the chemico-biological reactions, where it is customary to establish similar calculations and comparisons, such as those attributed to the respiration of living plants. The absorption of oxygen and the production of carbonic acid do not present in these beings the necessary correlation which exists in the higher animals, where nutrition and respiration constitute a cycle, in which, in the normal condition, the organism resumes a final state identical with its original condition.

Remarks on a Paper by M. Duner entitled "Is there Oxygen in the Solar Atmosphere?"—Prof. J. Janssen.—The method which M. Duner has employed in his important researches on the rotation of the sun—in which, moreover, he has not considered the question of the presence of oxygen in the sun—cannot in my opinion be regarded as capable, by itself, of elucidating the complex question which forms the subject of this paper.

Conclusions Respecting the Appearance of Light Coloured Parts and the Causes of the Greening of Oysters.—Ad. Chatin and A. Muntz.—1. The green colour of oysters is not due to chlorophyll. 2. The iron is especially localised in the branchial papillæ, the seat of the colouration in oysters, both green and brownish; its proportion increases with the intensity of the colour. 3. The black mud of the oyster beds owes its colour to the ferrous sulphide and oxide; it is a reductive medium rich in ammonia without any trace of nitrates or nitrites. 4. The black mud changes by oxidation into mud of an ochre colour, in which the ferrous sulphide and oxide are replaced by ferric oxide and sulphates, and the ammonia by nitrates and nitriles. 5. The oxidation is due, not merely to microbia, but to small green algæ, which give off nascent oxygen. 6. Calcium sulphate is found in a large proportion in the earth of the oyster beds. Calcium carbonate may be wanting. 7. Phosphoric acid exists in the proportion of 1 to 2 per 1000 as in good arable lands. 8. The proportion of nitrogen, generally from 1 to 1·5, has been found to reach 7·55 in the experimental vivarium at Roscoff.

Verbal Report on a Claim of Priority. — Henri Ulrich Dühring.—In the Session of November 27, 1893, Ulrich Dühring reclaimed priority in announcing a law on saturated vapours, indicated and verified by Edmond Colot (*Comptes Rendus*, cxiv., 653). The Commission recognises that this law had been previously announced by U. Dühring.

Obituary Notice.—The perpetual secretary announced to the Academy the loss which science had sustained in the person of Prof. H. R. Hertz, of the University of Bonn, who died on January 1, 1894, in his 37th year.

Composition of the Aqueous Solutions of Salts According to the Indices of Refraction.—Paul Bary. —If we admit the theory of Arrhenius it follows that the dissociated salts, as far as refraction is concerned, behave as if the dissociation did not exist.

Researches on the Chemical Action Exerted upon Wine by Naphthyl-calcium Sulphate (Abrastol).—Scheurer-Kestner.—It is very probable that abrastol may be advantageously substituted for plaster in the treatment of wines. A few grms. of abrastol per litre are sufficient to prevent all secondary or posterior fermentation. The absence of cardiac and cerebral disturbance during the ingestion of abrastol, its rapid elimination in the urine, and the remarkable toleration of the organism for this product, enable us to infer that this substance is inoffensive for the preservation of wines. The detection of foreign substances in abrastolised wines may be effected as if the abrastol were not present.

Presence of Poison Glands in Colubrine Serpents and on the Toxicity of their Blood.—C. Phisalix and G. Bertrand.—The species of serpents experimented upon were the water-snake (*Tropidonotus natrix*) and the Thuringian adder (*Tropidonotus viperinus*), a snake not met with in Britain. The blood of these serpents, if injected into the circulatory system of guinea-pigs, proves fatal, with symptoms similar to those produced by the bite of the viper.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xiii., No. 1.

Automatic Burette.— M. Guichord.— This memoir cannot be intelligibly reproduced without the accompanying illustration.

Preparation of Carbon under Strong Pressure.—Henri Moissan.—This paper requires the three accompanying figures.—The author has tried many experiments upon iron, but only a certain number have yielded small transparent crystals possessing all the characters of the diamond.

Preparation of Uranium at a High Temperature.—Henri Moissan.—By the direct reduction of uranium oxides with carbon at a high temperature, the author has obtained cast uranium. The author proposes to give the characteristic properties of this compound in a future communication.

Rapid Preparation of Chrome and of Manganese at a High Temperature.—Henri Moissan.—Both these preparations are effected by means of the electric furnace. For manganese there is required an arc measuring 100 ampères and 50 volts, acting for ten to fifteen minutes. The reduction of chromic oxide is more difficult. It requires a current of 350 ampères and 50 volts. The ingots obtained contain from 8·60 to 12·85 per cent of carbon. Native chrome iron may be employed as a raw material.

Lithium Fluoride.—C. Poulenc.—Lithium fluoride, LiF, by its slight solubility, its point of volatilisation, which is higher than that of potassium and sodium fluorides, and its crystallisation in octahedra under the influence of alkaline chlorides, tends to establish a transition between the alkaline and the alkaline-earthy fluorides. It is distinguished from the latter by not forming a fluochloride.

Production of Saccharose During the Germination of Barley and During the Ripening of Apples.—L. Lindet.—This paper is not suitable for abstraction.

A New Method for the Preparation of Methylamine, and on the Constitution of Hexamethylenetetramine.—MM. Trillat and Fayolat.—The formation of methylamine and ethylamine by this method depends on the reduction of the ammonium.

Determination of Nitric Nitrogen by means of the Nitrometer.—Emile Henry.—This paper requires the three accompanying figures.

MEETINGS FOR THE WEEK.

MONDAY, 29th.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "The Detection and Measurement of Inflammable Gas and Vapour in the Air," by Frank Clowes, D.Sc.
TUESDAY, 30th.—Royal Institution, 3. "Locomotion and Fixation in Plants and Animals," by Prof. Charles Stewart, Pres.L.S.
—— Institute of Civil Engineers. 8.
—— Society of Arts, 8. "The Adam Architecture in London," by Percy Fitzgerald, M.A.
WEDNESDAY, 31st.—Society of Arts, 8. "Californian Wines," by Charles F. Oldham.
—— British Astronomical, 5.
THURSDAY, Feb. 1st.—Royal, 4.30.
—— Royal Institution, 3. "The Life and Genius of Swift," by the Rev. Canon Ainger, LL.D.
—— Chemical, 8. "Note on the Liberation of Chlorine by the Interaction of Potassium Chlorate and Manganese Dioxide," by Prof. McLeod, F.R.S. "An Examination of some Recent Freezing-point Determinations," by S. U. Pickering, F.R.S. "The Salts of Dehydracetic Acid," by Dr. Collie, and H. R. Le Sueur, F.R.S. "A New Method of Preparing Carbon Tetrabromide," by Dr. Collie.
FRIDAY, 2nd.—Royal Institution, 9. "Bookbinding, its Processes and Ideal," by T. J. Cobden-Sanderson.
—— Geologists' Association, 7.30. (Anniversary).
—— Quekett Club, 8.
SATURDAY, 3rd.—Royal Institution, 3. "English Schools of Musical Composition," by Prof. W. H. Cummings.

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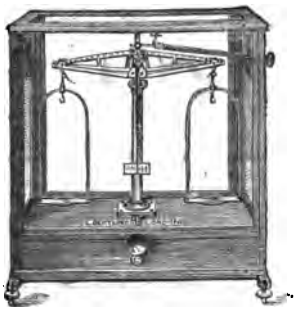

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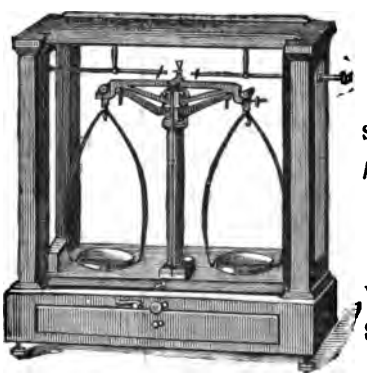

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MOLECULAR WEIGHTS.*

By Prof. W. RAMSAY, Ph.D., F.R.S.

In addressing you to-night I have first to thank you for the honour you have done me in asking me to be the first to wish prosperity to your newly-born Chemical Society. London is a vast place; "as far as East is from West," so difficult it is for many, if not all of you, to be present at meetings of the "Chemical Society of London." You have done well in starting a new one; I wish it as much prosperity and vigour as its elder sister; but may I venture to express the hope that it will never possess a Journal of its own, for to multiply Journals is to multiply sorrow; it would be better to enter into some agreement with one of the older Journals to publish your work. You will be more able thus to let your light shine before men, and you will save students of chemistry from the fatigue of consulting a new set of indexes. The literature of our science is growing beyond all bounds, and we should use every effort to concentrate it into a few channels.

I suppose that this Society will consist largely of those engaged in the commercial aspects of chemistry, and I perhaps owe an apology for bringing before you a subject apparently so remote from commercial interests as "molecular weights." But I may remind you that all industry depends on scientific principles, and he who is most at home in the fundamental principles of the science, and is able to apply them to the special problems of commerce, is most likely to win success in the fields of industry, if the bent of his mind turns in that direction.

I.

When Dalton discovered the laws of definite and multiple proportion, he was led to revive the ancient atomic theory to account for his facts. He imagined each element to consist of small homogeneous particles possessing definite weight, and he supposed compounds to be formed by the union of such particles with each other in certain ratios. I will remind you that, in assigning an atomic composition to water, he believed it to consist of an atom of hydrogen in union with an atom of oxygen. Why? Because, inasmuch as water was then the only known compound of these elements, he chose the simplest ratio as that in which the elements should combine—one atom of each. But we now know that water-gas actually consists of two atoms of hydrogen in union with one atom of oxygen. It was Avogadro who first pointed out that equal volumes of gases contain equal numbers of molecules, and who showed a means of reconciling Gay-Lussac's discovery of the fact that gases react in whole volumes, with Dalton's theory of atoms. Because water is formed by the union of two volumes of hydrogen with one volume of oxygen, it therefore consists of the products of union of two molecules of hydrogen with one molecule of oxygen. Avogadro pointed out, however, that by their union two molecules of water-gas are formed, and not one; yet, although these ideas were enunciated in 1811, it was not until Cannizzaro revived interest in the subject, in a masterly discourse delivered to the University of Genoa in 1858, that Avogadro's ideas gained general acceptance. Avogadro's law is now one of the axioms of chemistry and physics, and we all accept without hesitation the dictum that, by comparing the relative weights of equal volumes of two gases at equal temperature and pressure, we compare the relative weights of their molecules.

I have ventured to remind you of these elementary principles for completeness sake; I need do no more than allude to the ingenious processes of Gay-Lussac, Regnault, Hofmann, Dumas, and Victor Meyer, by means of which the relative weights of gases and vapours may be readily compared.

But before leaving the subject of gases, let us examine Avogadro's law from a somewhat different standpoint. Imagine two equal volumes of two gases, at the same temperature; unless we know the pressure we cannot compare the relative numbers of molecules in equal volumes; but if they are each under the same pressure, then we know that they each contain the same number. If the one gas is under twice as great a pressure as the other, it follows, from Boyle's law, that it contains twice as many molecules. Or, again, if two gases, which need not have the same volume, are at the same temperature, and if the numerical product of pressure and volume is equal for each, we are dealing with equal numbers of molecules; because as pressure increases, volume diminishes correspondingly, so that the product of the two remains constant if the number of molecules does not change,—that is, if no molecules are allowed to enter, or to escape from the containing vessel. And lastly, from Gay-Lussac's law, as equal volumes of all gases are equally increased by a definite rise of temperature, provided pressure remains constant, so if products of the pressures and volumes of two gases are equally increased by a definite rise of temperature, we know that they possess equal numbers of molecules. Stated in mathematical symbols, if p stand for pressure, v for volume, and T for absolute temperature of one gas, and p' and v' for pressure and volume of another, then—

$$\frac{p\,v}{T} = \frac{p'\,v'}{T},$$

if the two gases contain equal numbers of molecules.

II.

So far we have been considering matter in the gaseous state. The results of which I have been reminding you have been known for long; but a new development of theory has arisen within the last five or six years, enabling us to ascertain the relative weights of molecules, not merely in the gaseous state, but when dissolved in appropriate solvents. It is to J. H. van 't Hoff, the Professor of Chemistry at Amsterdam, that we owe the inception of this brilliant theory. As recently as the 16th of December last he gave a masterly sketch of the growth of his ideas, which I shall here try to reproduce for you; but in reproduction much of the neatness of expression is necessarily lost. His lecture is entitled "On Osmotic Pressure, from the point of view of Physiology, Physics, and Chemistry."

He was led to consider the question first in thinking over Berthelot's researches on the formation of esters, especially ethyl acetate. It is well known that on heating together a mixture of ethyl alcohol and acetic acid, the change which takes place is according to the equation—

$$C_2H_6O + C_2H_4O_2 = C_2H_3O_2.C_2H_5 + H_2O.$$

But if definite quantities of alcohol and acid be heated in a sealed tube the reaction is never complete; equilibrium results between the reagents and the products of reaction, so that, after all apparent change has ceased, all four substances are present.

This phenomenon has been explained by the supposition that action in the reverse direction also takes place, and this may be symbolised by the equation—

$$\text{Alcohol} + \text{acid} \rightleftharpoons \text{ethereal salt} + \text{water}.$$

The Norwegian chemists, Guldberg and his brother-in-

* An Address given to the People's Palace Chemical Society, at its Opening Meeting.

law Waage, in 1868, investigated many similar cases, and tried to calculate the quantities of all four reacting substances in the final product. Representing by p the weight of alcohol, and by q, r, and s the weight of acid, ethereal salt, and water respectively in unit volume, the force which tends to transform the original system of alcohol and acid into ethereal salt and water is proportional to the product $p\ q$. The state of equilibrium results from an opposing force, proportional to the product $r\ s$, which tends to reverse the reaction. It is also necessary to take account of the action of the alcohol on the ester, &c., and in denoting by K, K_1, &c., the coefficients of proportionality, they formulated the equation—

$$K\ p\ q = K_1\ r\ s + K_2\ r\ p + \&c.$$

Van 't Hoff, after the publication of Berthelot's experiments, attempted to formulate the action as the result of two *velocities* instead of two forces. He regarded the state of equilibrium as the resultant of two contrary rates of transformation, and thus obtained a somewhat simpler equation. The rate of transformation of the original system is evidently proportional to the weight of the alcohol, p, to the weight of the acid, q. Replacing the idea of "active mass," as Guldberg and Waage styled the weights of substances present, van 't Hoff made use of concentration, C, and obtained the equation—

$$K_1 C_{\text{(alcohol)}} \cdot C_{\text{(acid)}} = K_2\ C_{\text{(ester}} \cdot C_{\text{(water)}}.$$

But calculated thus the agreement, though approximate, was not satisfactory, and some flaw in the reasoning was suspected. In attempting to obtain greater concord, van 't Hoff supposed that the number of encounters of molecules of alcohol with molecules of acid is proportional to the concentration. Supposing the methods of thermodynamics be employed, and the principle of a reversible cycle (Carnot's engine) be applied; supposing the four substances—alcohol, acid, ester, and water—to be in the gaseous state, and Boyle's, Gay-Lussac's, and Avogadro's laws be applied, the equation just mentioned is reproduced.

Here the theory of osmotic pressure is touched. It involves the question, Can Carnot's principle be applied to dilute solutions? or, in other words, Is it possible to produce with solutions reversible operations?

Van 't Hoff's attention was next called to the botanist De Vriess's experiments on the cause of withering of plants. The plant-cells consist of a wall surrounding a soft protoplasmic matter, containing a certain quantity of sugar and salts. When the cell is swollen the cell-wall touches the protoplasm, but when the flower is faded the protoplasm contracts away from the cell-wall. On plunging the flower into water the cell fills, and the flower recovers its bloom. This is due to the fact that water enters the cell-walls, owing to the attraction of the contained salts. The wall possesses the property of retaining salts while allowing water to pass. When the flower is dead the cell-walls lose this property. By plunging a living flower into strong salt solution the water passes outwards through the cell-walls, and the plant droops. On replacing it in water the cells swell, and the plant revives. It is possible to choose salt solution of such strength that no water enters or leaves the cell. Such a solution is said to be "isotonic" with the salt in the interior of the cell. It is also possible to compare different salts with each other, and to note the concentrations at which they are isotonic with the contents of the cell, and therefore with each other.

Similar experiments can be made with that animal cell, a blood corpuscle; or with the large cell, the animal eye.

The botanist Pfeffer has endeavoured to imitate such natural phenomena in constructing an artificial cell of porous clay, the interstices in the walls of which were filled with a gelatinous precipitate of copper ferrocyanide. Filling such a cell with a 1 per cent solution of sugar and plunging it into water, the water was attracted through the walls of the cell, and a small pressure gauge connected with the cell registered an increase of pressure in the interior of the cell. This pressure was found to be higher, the higher the temperature. With a 1 per cent solution of sugar at 6·8° in the cell, the pressure rose to about two-thirds of an atmosphere.

This operation can be reversed. Suppose pressure applied to the mercury in the manometer, water could be forced out of the cell, and the solution of sugar contained in it could be concentrated. A cycle of operations can thus be carried out similar to that imagined by Carnot, and the principles of thermo-dynamics can be then applied.

Pfeffer showed that the osmotic pressures in such a cell are proportional to the concentration. Now concentration may be defined as a number of molecules in unit volume; and thus a law analogous to that of Boyle is arrived at, in which an increase of numbers of molecules in unit volume is accompanied by corresponding increase of pressure. Similarly an increase of temperature produces an increase of osmotic pressure similar and equal to the increase of gaseous pressure which the same rise of temperature would produce in a gas; and here we have a law analogous to that of Gay-Lussac. Here, then, an equation similar to the gas equation $PV = RT$ may be applied; and if pressure be measured in grms. per square c.m., volume in litres, and if T denote degrees on the absolute scale, we find for atmospheric pressure and 0° C. = 273° absolute—

$$10{,}333 \text{ grms.} \times 22{\cdot}39 \text{ litres} = 273° \times 846.$$

The value of R in the above equation is therefore 846.

In applying the laws of thermo-dynamics to the equation representing the action between alcohol and acetic acid, it must be remembered that the isotonic coefficients are proportional to the pressures exercised by molecular quantities of the dissolved substances. Now if molecular quantities be compared, taking equal volumes at equal temperatures, the value of R is proportional to the osmotic pressure and proportional to the isotonic coefficient. The equation—

$$K_1 C_{\text{(alcohol)}} \cdot C_{\text{(acid)}} = KC_{2\ \text{(ester)}} \cdot C_{\text{(water)}}$$

changes therefore to—

$$K_1 C^{i\ \text{(alcohol)}}_{\text{(alcohol)}} \cdot C^{i\ \text{(acid)}}_{\text{(acid)}} = K_2 C^{i\ \text{(ester)}}_{\text{(ester)}} \cdot C^{i\ \text{(water)}}_{\text{(water)}},$$

where i stands for "isotonic coefficient." This formula applies equally well to solutions; and van 't Hoff adduces an application to results relating to the solubility of magnesium carbonate in carbonic acid, worked out in detail by Schlœsing and Engel, which corroborate the theory stated.

But it is possible to calculate from the osmotic pressure, the concentration, and the temperature of a solution of sugar, the value of R in the same manner as it can be deduced for a gas. For a 1 per cent solution at 6·8° the values are as follows:—

$$P = 10{,}333 \times \tfrac{1}{34}.$$
$$V = 34{\cdot}2 \text{ litres; and } R = 846, \text{ nearly.}$$
$$T = 288{\cdot}8.$$

Here the molecular weight of sugar is assumed as corresponding to the formula $C_{12}H_{22}O_{11}$, viz., 342; but knowing R it is obvious that by transforming the equation, a measurement of osmotic pressure, together with a knowledge of the temperature and of the value of R would enable us to calculate the molecular weight.

The osmotic pressure of a solution of sugar is equal to that which it could exert were it possible, without changing concentration, to transform it into a gas and remove the solvent.

That this theory is well founded and leads to other important laws is shown by the following considerations:—

When two solutions are isotonic they possess the same vapour-pressures. To demonstrate that this is the case let us imagine a hollow ring divided into two portions by

a partition—allowing water only to pass—crossing its lower part; on one side of this partition let there be a solution of cane-sugar, and on the other one of common salt, isotonic with each other, but exerting different vapour-pressures. Then water vapour could distil round the upper part of the ring, increasing the level of one of the solutions. The concentration of that solution would diminish; it would cease to be isotonic with the other solution, and water would pass through the porous partition to restore equilibrium. Perpetual motion would thus be engendered, which is impossible. Hence two isotonic solutions have equal vapour-pressures.

Other similar relations are—that two isotonic solutions have the same boiling-point, and that they possess the same freezing-point as shown by De Vriess. The isotonic coefficients are directly proportional to the molecular depressions measured by Raoult.

This can be proved as follows:—In a vessel containing water place upright a tube, the lower end of which is closed by a semi-permeable membrane containing a solution of sugar. When equilibrium has become established the solution of sugar will have risen in the tube to a certain height, H. The vapour-pressure of the solution is obviously equal to that of the water, less the pressure of the column of water-vapour, H. The osmotic pressure, on the other hand, is represented by the column of liquid of the same height, H. We have thus the proportion—

$$\frac{\text{Osmotic pressure}}{\text{Diminution of pressure}} = \frac{\text{Density of solution}}{\text{Density of vapour}}.$$

The densities may be calculated from known data, and the osmotic pressure may be calculated, taking R as 845; and this leads to the very simple result $\frac{\text{Diminution of pressure}}{\text{Pressure}}$ × molecular weight of dissolved substance = 1-100th of molecular weight of solvent. This relates to a solution of 1 per cent.

Here we have a statement of Raoult's law.

It is also easy to calculate, in absolute value, the diminution of pressure, and the rise of boiling-point, Δt, produced by the solution of a compound in a liquid; the equation is—

$$\Delta t \times M = \frac{0{\cdot}02\,T^2}{L},$$

where M is the molecular weight, T the boiling-point on the absolute scale, and L the heat of vaporisation of the solvent.

Lastly, an analogous relation may be deduced for the lowering of freezing-point Δf, viz.,—

$$\Delta f \times M = \frac{0{\cdot}02\,T^2}{W},$$

where W here represents the heat of liquefaction of the solvent. The product $\Delta f \times M$ is the molecular lowering of melting-point observed by Raoult in many cases. In these equations Δt, Δf, T, L. and W may all be experimentally determined, and from their found values M may in each case be calculated.

We cannot spare time to-night to follow van 't Hoff in his remarks on the osmotic pressures of salt-solutions; how they are in many cases twice as great as one would expect them to be, provided the salt experimented on is expressed by what we may term, with Dalton, a "binary" formula,—*i. e.*, salts like NaCl, KBr, $Ag(NO_3)$, &c.; how such behaviour has been found concordant with their electric conductivities, and Arrhenius's explanation of electrolysis. Such considerations would need several lectures. I will merely ask you to observe that, so far, the magnitude of gaseous molecules and of molecules in solution has been ascertained, and I will ask you now to follow me in considering the magnitude of molecules of liquids, as such.

III.

When a liquid rises in a capillary tube it does so in virtue of what is termed its surface-tension; the molecules on its surface attach themselves to the glass tube, and exert force on each other. It is this force which causes the ascent of the liquid. Now just as we can measure the work done in *compressing* a gas by multiplying a force, pressure, by a quantity, volume, so we can measure the work done in *stretching* a liquid by the product of this force, surface-tension by surface, a quantity. The greater the force the higher the liquid will ascend in the capillary; the lighter the liquid the higher it will ascend; the narrower the capillary tube the higher it will ascend. We can measure this force, therefore, by multiplying half the radius of the tube by half the height to which the liquid ascends. and by the density of the liquid; and we can reduce the product to dynes, or units of force, by multiplying by g, the force of gravity at the latitude at which the experiments are made. We thus we get the equation—

$$\gamma = \tfrac{1}{4}\, r\, g\, h\, \rho,$$

where γ stands for surface-tension, r for the radius of the tube, g for 981—the gravity constant, h for the height of ascent of the liquid, and ρ for the density of the liquid.

Density or specific gravity may be defined as the weight of unit volume; and specific volume as the reciprocal of density, or the volume of 1 grm. Now conceive a cube; the cube-root of a cube is a line, and the square of the cube-root is the surface bounding one of the sides of the cube. If v is the volume of such a cube, weighing 1 grm., $v^{\frac{2}{3}}$ is the area of the surface of one side of such a cube. By multiplying the surface-tension of a liquid by its specific volume raised to the two-thirds power, we obtain the work required to create such a surface. This we may term surface-energy.

Now, it is found that the surface-energy of a liquid, instead of increasing with rise of temperature, like the volume-energy or pv. of a gas, decreases; and for many liquids, indeed I imagine for most, the rate of decrease varies uniformly with the temperature, so that a rise of 10° at one part of the thermometric scale produces a decrease equal to that which a rise of 10° at another part of the scale would do.

Although we do not know the actual number of molecules in any gas, yet we know, from Avogadro's law, that a litre of hydrogen contains as many molecules as a litre of oxygen, at equal temperature and pressure. Suppose we condense two gases to the liquid state, the molecules may unite in twos or in threes, or they may remain unpaired. Imagine them to remain unpaired; then the liquid resulting from each of two gases will contain equal numbers of molecules. The two liquids, however, need not have equal volumes. Suffice it to state that the volumes of liquid obtainable from 22·36 litres of gas (that capable of containing the molecular weight of the substance expressed in grms.) are termed their *molecular volumes*. The molecular volumes of two liquids, therefore, contain equal numbers of molecules, provided the molecules do not unite in twos or threes or fours, in virtue of their condensation, on assuming the liquid state. The two-thirds power of the molecular volumes, as shown by Eötvös, will represent the molecular surfaces; that is, surfaces on which equal numbers of molecules are distributed, provided they are distributed evenly on the exterior and in the interior of the liquid. And by multiplying this molecular surface by the surface-tension of the liquid, we obtain the molecular surface-energy; that is, the energy required to stretch a surface over which a definite number of molecules are distributed.

Just as the surface energy decreases with rise of temperature, so the molecular surface energy decreases. Multiplying by the molecular surface instead of the surface changes merely the value of the number standing for the rate of change; and the important law becomes evident—that the change on equal rise of temperature is equal,

or very nearly equal, for equal numbers of molecules. Hence a rise of one degree diminishes the molecular surface-energy by about 2·1 ergs or units of energy, just as raising the temperature of a gas of constant volume at 0° by one degree increases its volume energy by 1/273rd.

Mathematically expressed, this may be represented thus:—

$$K = \frac{\gamma(M v)^{\frac{2}{3}} - \gamma'(M' v')^{\frac{2}{3}}}{t' - t};$$

where K is the coefficient of change, 2·1, γ and γ' the surface-tension at two temperatures, $(M v)^{\frac{2}{3}}$ and $(M' v')^{\frac{2}{3}}$ the molecular surfaces at the same two temperatures, and t and t' those temperatures.

In this way, in conjunction with Dr. John Shields, I have investigated the molecular constitution of a great number of liquids, and, as a rule, these turn out to be mono-molecular; that is, the molecules in the liquid state are not more complex than in the state of gas; they do not unite in twos or threes or fours, but remain simple. Thus CCl_4 is the formula of liquid chloride of carbon, as of gaseous; C_6H_6 is the formula of both liquid and gaseous benzene, and so on.

But there are other liquids in which the value found for R is not 2·1, but a smaller number, and, moreover, it changes with rise of temperature, increasing, and in some cases nearly equalling 2·1. This obviously points to the fact that the complex molecules are splitting up as the temperature rises; in fact the deduction is similar to that which we draw when a gas, like that of nitric peroxide, decreases in density with rise of temperature; we say that complex molecules of N_2O_4 are being decomposed into simple molecules of NO_2.

It is possible, on the assumption that this change is not a very rapid one, to calculate the molecular weight of such an associating liquid, and to find how many molecules, on the average, have associated to form molecular groups. To do so requires merely a transformation of the equation already given; and we obtain—

$$M = \left\{\frac{K(t' - t}{\gamma v^{\frac{2}{3}} - \gamma' v'^{\frac{2}{3}}}\right\}^{\frac{3}{2}}.$$

The liquids which show complex molecules are, as a rule, those which contain hydroxyl; the alcohols, phenol, water, nitric and sulphuric acid, and the organic acids, such as acetic; but there are a few others, among which are to be found propionitrile, and nitroethane; the presence of nitrogen appears sometimes to favour the coalescence of simple into complex molecules.

As regards the complexity, it may be of interest to note that acetic acid, about its melting-point, consists of molecules formed by the union of four gaseous ones; that ethyl alcohol at ordinary temperature has for the most part the formula $(C_2H_6O)_3$, and that water is $(H_2O)_4$ near its freezing-point. Nitric acid consists mostly of double molecules.

But the most curious substance is sulphuric acid. Its molecular weight as a liquid appears to be $(H_2SO_4)_{32}$ between 10° and 130°; above 130°, however, the complex molecules rapidly break down, and at 280° they are reduced in complexity to about $(H_2SO_4)_3$.

I have tried to show you how it has been possible to determine the relative weights of molecules in the gaseous state, where they are widely separated from one another; in the state of solution, where, again, their distance is increased by separating them from each other by interposing molecules of a solvent; and lastly, their attraction for each other to form a surface-film has been made the means of measuring the relative weights of molecules in the liquid state. It still remains to find some method by which the molecular weights of substances in the solid state can be ascertained; it is surely possible; probably the way lies open if we only saw it, and the discovery will be full of interest.

ON CERIC BICHROMATE AND THE SEPARATION OF CERIUM FROM LANTHANUM AND DIDYMIUM.

By G. BRICOURT.

Erk has studied the action of the electric current upon cerous salts, and shown that in certain cases there may be deposition of a salt or of ceric oxide at the positive pole. Thinking that this property might be available for separating cerium from lanthanum and didymium, I have repeated his experiments and have made successful use of a chromic solution which has also furnished a cerium bichromate not as yet examined.

Into a slightly acid solution, obtained by dissolving cerous carbonate in chromic acid, I passed a current of 2·5 to 3 volts, using as positive pole an electrode with a large surface.

When the current was closed there was immediately produced at this pole a crystalline deposit, which, when freed from the mother-liquid, washed, and dried, corresponded to the formula $CeO_2,2CrO_3,2H_2O$.

This substance takes the form of brilliant orange-red crystals. It is soluble in acids, and gives the reactions of the ceric salts. Water, in which it is quite insoluble, decomposes it slightly in the cold, but very rapidly on ebullition, and converts it into a yellow chromate, which on prolonged digestion gives up all its chromic acid and leaves a residue of ceric hydroxide.

Separation of Cerium from Lanthanum and Didymium.

Lanthanum and didymium, which do not form higher oxides with oxygen, if treated in a similar manner give no deposit at the positive pole. Upon this property we may found a process for their separation.

To decide upon its value, I treated as above the commercial oxides extracted directly from cerite. The bichromate obtained was well washed, dissolved in hydrochloric acid, and the cerium was thrown down as an oxalate. A very concentrated nitric solution of the latter salt on examination with the spectroscope gave no trace of an absorption ray. Another portion on ignition yielded cerium oxide of a very pale yellow colour. From these two experiments we may infer the purity of the salt.—*Comptes Rendus*, cxviii., p. 145.

SEPARATION OF VANADIC ACID FROM CHROMIC ACID.

By VALERIAN von KLECKI.

We find vanadium in ores always associated with ferric oxide, alumina, manganese, and frequently with chrome. The quantitative determination of vanadium, in ores, slags, &c., presents various difficulties, since the methods for its analytical separation are as yet but little developed, especially those of special interest for the analysis of the native vanadiates. This especially affects the separation of vanadium from chromium—a task involving great difficulties on account of the analogous behaviour of both these elements with reagents. Thus the barium, mercury, and lead salts of both elements are insoluble, whence their separation in this manner is scarcely possible. Ammonia precipitates chromium (as chromic oxide), and vanadium as sulphide.

Lindemann, who examined a chromiferous hydroferrite from the neighbourhood of Salzgitter, was compelled to overcome the difficulties of separating chrome and vanadium by a troublesome and circumstantial procedure. In the meantime, this separation seems practicable by a method which Carnot recommended for the determination of vanadic acid.

The vanadic acid is precipitated by means of uranium salts from a solution either neutral or slightly acidulated

with acetic acid, boiled; the yellow precipitate is filtered, washed, ignited, and weighed. The composition of the ignited precipitate is $V_2O_5 2VO_3$. At first sight this method does not seem applicable for the separation from chromic acid, as this acid is also precipitated by uranium salts. I found, however, that whilst uranium vanadate is insoluble in acetic acid, one drop of acetic acid is sufficient to dissolve the uranium chromate. In order to test the method, I effected three analyses, proceeding as follows:—A weighed quantity of ammonium vanadate was dissolved in water in a porcelain capsule along with a weighed quantity of potassium chromate; the solution was mixed with a calculated weighed quantity of uranium nitrate, more than sufficient for precipitation, and boiled after the addition of a few drops of acetic acid. After the precipitate had been allowed to subside for twelve hours, it was filtered and well washed with distilled water. A drop of the filtrate mixed with potassium ferrocyanide gave a brown colour, which indicated an excess of uranium nitrate. The reaction of the filtrate was faintly acid. The precipitate was dried and ignited, leaving a black crystalline powder. The quantity of vanadic acid was calculated from the weight of the precipitate. In the filtrate the chromic acid was determined either by precipitation with mercurous nitrate and weighing the chromium oxide, or by titration with ferrous ammonium sulphate.—*Zeitschrift für Anorganische Chemie*, v., 381.

OZONE IN THE LIGHT OF THE PERIODIC SYSTEM.

By A. WALKOWICZ.

Without entering more closely into the voluminous literature of ozone, I wish to point out the importance of considering this substance in the light of the periodic system. If we reflect that the members of the sixth group show with oxygen (or with hydroxyl groups) a valence lower than the members of the seventh group with reference to the composition of the haloid-oxy-acids, the following formulæ may be theoretically deduced for the compounds of the elements of the oxygen group, O, S, Se, Te:—

$$H_2RO,\ H_2RO_2,\ H_2RO_3,\ H_2RO_4;$$

or for their anhydrides,—

$$R,\ RO,\ RO_2,\ RO_3.$$

If in the above formula were substituted for R, O or S we have—

$$H_2OO,\ H_2OO_2,\ H_2OO_3,\ H_2OO_4$$
$$HSO,\ H_2SO_2,\ H_2SO_3,\ H_2SO_4$$

and for the anhydrides:—

$$O,\ OO,\ OO_2,\ OO_3$$
$$S,\ SO,\ SO_2,\ SO_3$$

If we turn to ozone, recognised as a modification of oxygen, its formula, according to the above conspectus, must be $O\,O_2$; whence it is the anhydride of the unknown acid, H_2OO_3—just as SO_2 is the anhydride of H_2SO_3. Hence ozone is in its constitution analogous to SO_2, and consequently its properties display analogies with those of the corresponding oxides of the other members of the oxygen-sulphur group.

According to the formula—

$$\begin{matrix} S & = & O \\ & = & O \end{matrix}$$

the oxygen in ozone must occur partially as quadrivalent, and be combined with two bivalent oxygen atoms which have consequently not equal rights. Ozone—

$$\begin{matrix} O & = & O \\ & = & O \end{matrix}$$

and sulphurous acid—

$$\begin{matrix} S & = & O \\ & = & O \end{matrix}$$

are gases; selenious acid, SeO_2, and tellurous acid, TeO_2, are solids, readily volatilised if heated; all have a peculiar odour, which decreases as the molecular weight rises.

An aqueous solution of ozone is very readily dissociated at the ordinary temperature, H_2SO_3 is not stable in hot water, SeO_2 forms a very stable acid, H_2SeO_3, and H_2TeO_3 is a solid.

Ozone and SO_2 discharge colouring-matters. Sensitive litmus paper is bleached by concentrated ozonised water, but before the complete decolourisation there appears a peculiar shade resembling indistinct reddening by an acid.

Manner of Formation.—SO_2, SeO_2, and TeO_2 are usually produced by directly heating the element in question in an atmosphere of oxygen. Hence it must be expected that on every every combustion in an O atmosphere, and on an electric discharge,—

$$\begin{matrix} O & = & O \\ & = & O \end{matrix}$$

must be formed, which is actually the case.

The isolation of H_2SO_3 corresponding to SO_2 has not yet been effected. In like manner we must fail to effect the production of the more unstable oxygenous acid, H_2OO_3. On the other hand, as H_2SO_3 forms fairly permanent salts, it is possible that the unknown H_2OO_3 forms salts of the type M_2RO_3, M_2OO_3, or M_2O_4. In fact, we know potassium tetroxide, K_2O_4, which, in accordance with the above consideration, is analogous to the sulphites, an oxygenite of the structure—

$$\begin{matrix} KO \\ KO \end{matrix}\!\!>O = O,$$

analogous to—

$$\begin{matrix} KO \\ KO \end{matrix}\!\!>S = O.$$

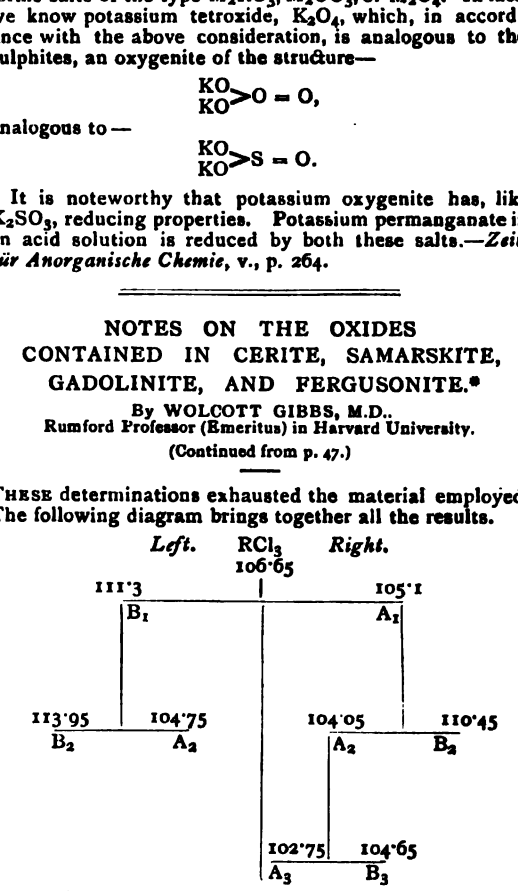
It is noteworthy that potassium oxygenite has, like K_2SO_3, reducing properties. Potassium permanganate in an acid solution is reduced by both these salts.—*Zeit. für Anorganische Chemie*, v., p. 264.

NOTES ON THE OXIDES CONTAINED IN CERITE, SAMARSKITE, GADOLINITE, AND FERGUSONITE.*

By WOLCOTT GIBBS, M.D.,
Rumford Professor (Emeritus) in Harvard University.

(Continued from p. 47.)

These determinations exhausted the material employed. The following diagram brings together all the results.



The diagram in the case of the oxides from cerite and monazite shows very clearly that, as with the oxides from

* *American Chemical Journal*, xv., No. 7.

gadolinite, the atomic masses B_1, B_2, B_3 increase, while those of A_1, A_2, A_3 diminish, but at a different rate, perhaps, as already remarked, because the conditions were not precisely the same. It seems very desirable that similar experiments should be made with the basic-nitrate process, which has been so much used, so as to determine which method gives results that converge most rapidly toward the atomic masses of pure oxides. Only in this manner can the relative values of the two methods be determined. I consider it probable that further experience with the oxychloride process will lead to a very material shortening of the process. I have employed for the most part porcelain crucibles holding about 130 c.c., but with larger muffles it would be easy to work up a kilogrm. of oxides at each operation. Also much is to be expected from a judicious mixture of the different products on the right and left having nearly the same atomic masses. All points fairly considered, I am I believe justified in offering the oxychloride process as worthy of further trial.

It appeared possible that basic bromides might be more advantageous than basic chlorides as means of differentiation, but the experiments made were not conclusive on this point. Observing the formation of beautiful, well defined crystals when the oxides from gadolinite and the cerite and monazite residues were dissolved in chlorhydric or bromhydric acid, and the solutions evaporated to a syrupy consistence, I examined two cases. The perfectly colourless and easily soluble crystals obtained from gadolinite earths free from cerite earths by chlorhydric acid after two successive crystallisations were analysed.

(111). 0·3248 grm. gave 0·1293 grm. C_2O_3=39·82 p.c.
(112). 0·3000 „ 0·1450 „ R_2O_3=48·34 „

The atomic mass is 107·10, so that the crystalline chlorides contained the earths in the same proportion in which they were obtained from gadolinite after separation of the cerite earths.

Precisely the same result was obtained with crystallised bromides prepared by dissolving the crude oxides from the cerite and monazite residues in bromhydric acid and evaporating. The beautiful colourless crystals were not quite free from the mother-liquor. Of these crystals,

(113). 0·3418 grm. gave 0·1064 grm. C_2O_3=31·11 p.c.
(114). 0·4266 „ 0·1325 „ C_2O_3=31·07 „
(115). 0·6110 „ 0·2879 „ R_2O_3=47·13 „
(116). 0·6896 „ 0·3293 „ R_2O_3=47·02 „

The atomic mass is 139·55, which is nearly the same as that obtained from the oxides directly, 137·25.

The mother-liquor from the crystals was also analysed.

(117). 0·3750 grm. gave 0·1171 grm. C_2O_3=31·25 p.c.
(118). 0·3237 „ 0·1015 „ C_2O_3=31·37 „
(119). 0·6752 „ 0·3180 „ R_2O_3=47·10 „
(120). 0·8150 „ 0·3837 „ R_2O_3=47·08 „

The atomic mass corresponding is 138·45. From the above it appears that little, if anything, is gained by crystallisation of the chlorides and bromides, at least in the cases cited.

The fact that potassic and sodic sulphates which do not give precipitates of double sulphates in cold saturated solutions of certain earths often give crystalline precipitates on boiling, has doubtless been observed. I do not find, however, that such observations have been noted in published papers. The following analyses will serve to show that valuable results may sometimes at least be obtained by this process.

A quantity of oxides from Samarskite, sent me by Dr. Shapleigh, was dissolved in chlorhydric acid and precipitated cold by an excess of potassic sulphate. After filtering off the double sulphates, sodic sulphate was added and the solution boiled. An abundant white crystalline salt was obtained. After washing with a little boiling water the double salt was dissolved in chlorhydric acid, and oxalic acid added after large dilution. The oxalates were converted into oxides, and these re-dissolved in chlorhydric acid and again precipitated with oxalic acid. The oxalates were then analysed.

(121). 0·2853 grm. gave 0·1217 grm. R_2O_3.
(122). 0·3889 „ 0·1660 „ R_2O_3.
(123). 0·5558 „ 0·2256 „ C_2O_3.

Atomic mass 89·55, which does not sensibly differ from the received atomic mass of yttrium. From this it appears that yttria was separated in quantity by one operation after the separation of the cerite oxides.

Application of the Cobaltamines to the Separation of the Oxides. — Many experiments were made to determine whether the sulphates of organic alkaloids would form double salts with the sulphates of the rare earths which could be made available for separations. These did not lead to satisfactory results, though double salts were formed in some cases. It then occurred to me that the sulphates and other salts of various cobaltamines, on account of their disposition to form highly crystalline compounds, might be employed with advantage. Following are the results of this investigation.

A solution of sulphate of luteocobalt precipitates completely from their cold solutions as neutral sulphates the four cerite earths now known, namely, the oxides of cerium, lanthanum, praseodymium, and neodymium. The double sulphates are beautifully crystalline, have an orange-red colour, and are very slightly soluble in cold water, but, practically at least, insoluble in boiling water. They are soluble in acids, and sometimes crystallise from weak acid solutions. All these compounds appear to have the same constitution, which is that of the salts discovered many years since by myself, and analysed in my laboratory by C. H. Wing (*Am. Journ. Sci.* [2], xlix., 363). I find, however, that the constitution of both the luteo- and roseo-salts may be much more accurately represented by the formulæ—

I. $2\{Co_2(NH_3)_{12}(SO_4)_3 + Ce_2(SO_4)_3\} + 3$ aq.
II. $2\{Co_2(NH_3)_{12}(SO_4)_3\} + 3\{Ce(SO_4)_2\} + 3$ aq.
III. $2\{Co_2(NH_3)_{10}(SO_4)_3 + Ce_2(SO_4)_3\} + 9$ aq.
IV. $2\{Co_2(NH_3)_{10}(SO_4)_3\} + 3\{Ce(SO_4)_2\} + 9$ aq.

Mr. W. J. Karslake has arrived independently at the same formulæ, and has calculated the percentages as required by them.

For Formula I.:—

		Calculated.	Found,
$24NH_3$	408	16·93	16·75 (loss)
4Co	236	9·79	9·31
4Ce	560	23·24	24·10
$12SO_4$	1152	47·80	47·77
$3H_2O$..	54	2·24	2·07
	2410	100·00	

For Formula II.:—

		Calculated.	Found.	
$24NH_3$ ..	408	17·97	17·73 (loss)	
4Co ..	236	10·40	10·80	10·74 10·44
3Ce ..	420	18·57	16·90	17·27 17·54
$12SO_4$ ..	1152	50·75	51·80	51·83 52·22
$3H_2O$ ..	54	2·37	2·47	2·21 2·39
	2270	100·00		

For Formula III.:—

		Calculated.	Found.	
$20NH_3$	340	14·72	14·24 (loss)	
4Co	236	10·22	10·39	9·60
3Ce	420	18·18	18·18	19·36
$12SO_4$	1152	49·86	49·73	49·97
$9H_2O$	162	7·02	7·00	7·31
	2310	100·00		

For Formula IV. :—

		Calculated.	Found.
$20NH_3$	340	13·88	15·13 (loss)
$4Co$..	236	9·64	9·90
$4Ce$..	560	22·85	20·99
$12SO_4$	1152	47·02	47·23
$9H_2O$	162	6·61	6·75
	2450	100·00	

The analyses are those of Wing.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 18th, 1894.

Dr. ARMSTRONG, President, in the Chair.

MESSRS. J. E. Brockbank, Charles Sordes Ellis, William Hatten Grieve, and Claude Vautin were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Good Boul, M.A., Churcher's College, Petersfield; Herbert Edward Burgess, 144, Warwick Street, Eccleston Square, S.W.; Herbert Henry Dains, 3, Cantonment, Vizianagram, Madras Presidency; Basil Leonard Dunne, 64, Lower Leeson Street, Dublin; Joseph Addey Fawcett, 153, Malpas Road, Brockley, S.E.; Edward Stanley Hayward, 23, St. Thomas Street, Winchester; Isaac Henry Heap, Fern Bank, Aynsley Road, Stoke-on-Trent; Francis Herbert Jennison, c/o A. Delingworth, Moscow, Russia; E. W. Lucas, 225, Oxford Street; Harvey Ernest Spillard, 5, Belitha Villas, Barnsbury Park.

Of the following papers those marked * were read :—

*98. "*The Molecular Formulæ of some Liquids as Determined by their Molecular Surface Energy.*" By EMILY ASTON, B.Sc., and WILLIAM RAMSAY, Ph.D., F.R.S.

The molecular surface energy and its variation with temperature of phenol, bromine, nitric acid, sulphuric acid, phosphorus, and nitrotrichloromethane have been determined by the authors by the method described by Ramsay and Shields (*Trans.*, 1893, 1089). The data given make it possible to calculate the molecular weights of the substances in the liquid state.

Phenol, as might be expected from its analogy with alcohol, is an associating substance; but as it possesses a fairly high molecular weight, the degree of association is not great; the results serve to suggest that between 46° and 78° it possesses the mean molecular weight 133·5, while in the state of gas its molecules have the weight 94.

Bromine, apparently, is somewhat more condensed than the formula Br_2 would imply, the number found being 202·8 instead of 160, between 10·6° and 46°.

Nitric acid, instead of possessing the molecular weight 63, has a molecular complexity corresponding to the weight 105·9 between 11·6° and 46·2°. This value approximates to that corresponding to the formula $H_2N_2O_6$.

Sulphuric acid shows a remarkable behaviour. From atmospheric temperature to 132·5° its molecule, apparently, is approximately thirty-two times as complex as the formula H_2SO_4 would imply; above 132°, however, dissociation rapidly ensues, and between 227° and 281° the molecule is only 2·8 times as complex as the formula H_2SO_4 implies.

The molecules of phosphorus in the liquid state, like those of the gas, have the formula P_4.

Chloropicrin, $CCl_3(NO_2)$, has a normal molecular weight. This result stands in opposition to that afforded by nitroethane, which shows signs of association.

DISCUSSION.

Mr. PICKERING said that the importance of obtaining various methods of determining the molecular complexity of substances in the liquid condition could scarcely be overrated; but he thought that it would be premature to attach implicit faith to the results obtained by Professor Ramsay's method until the discrepancies between the values given by it and other methods were explained or removed. The results which Professor Ramsay had obtained in some cases showed that it would be unwise to place too much confidence in his method at present, for he had found that a considerable number of substances gave values which, though constant throughout a wide range of temperature, yet indicated molecular weights which were not integral multiples of the formulæ weights.

The authors' results in the case of sulphuric acid were of interest in connection with those he had arrived at by determining the densities of solutions of this substance: from the peculiarity of the figure formed on plotting out their values (these forming a straight line throughout a considerable range, and a well-marked curve throughout the rest of the range), the authors concluded that $32H_2SO_4$ might represent the state of aggregation of the acid, whereas his results pointed to $36H_2SO_4$ (within experimental error the same degree of complexity), the lowest hydrate of which he had obtained indications containing acid and water in the ratio 36 : 1; moreover, in all the other low hydrates the acid molecules were present as simple submultiples of 36.

Mr. RODGER said there were two points in connection with Professor Ramsay's paper to which attention might be drawn. The first was of historical interest and referred to the work of Eötvös, which did not seem to be given the prominence which it deserved. In 1885 Eötvös showed that over wide temperature ranges K, the rate at which molecular surface energy varied with the temperature, was practically the same for liquids of different chemical natures, and these substances he held to be of the same molecular complexity in the states of gas and liquid. For the acids, alcohols, and water, K varied with the temperature and the chemical nature, and in such cases Eötvös concluded liquid molecular complexes were present. The equation which Eötvös *derived* by integrating the differential equation above mentioned only differed from the corresponding expression given by Prof. Ramsay in that it does not accurately indicate the temperature limits at which it breaks down.

Eötvös's method of estimating complexity is identical, however, with that of Professor Ramsay, and so far as they go his observations lead to like results. For these reasons, should the credit of instituting this method not be ascribed to Eötvös

The second point referred to the validity of the method. In the first place, neither Ramsay nor Eötvös had succeeded in placing the method on a firm theoretical basis. Eötvös's expression was deduced from van der Waals's generalisation that for two substances, A and B, in corresponding states,—

$$\frac{P_A V_A}{T_A} = \frac{P_B V_B}{T_B},$$

where P, V, and T are respectively the pressure, molecular volume, and temperature. In criticising Eötvös's method (*Zeit. Phys. Chem.*, 1893) Professor Ramsay has characterised this relation as false, and although in the light of Young's recent work this is, perhaps, going too far, its agreement with experimental results is not sufficiently close to be regarded as a proof that K is really a measure of complexity. By way of such a proof Professor Ramsay has pointed out that inasmuch as the rate of change of the molecular volume energy of a perfect gas is the same for all gases, provided they contain molecules of the same

degree of complexity, probably the rate of change of the molecular surface energy of a liquid is also the same for all liquids which are of the same molecular complexity. This can hardly be regarded as a proof, however, because the gas equation breaks down as soon as the gas is compressed—as soon, that is, as the molecules come within the sphere of each other's attraction, and it is precisely this attraction which is involved in the phenomena of surface energy. How is it possible, therefore, to draw any satisfactory conclusion from the behaviour of a perfect gas regarding the molecular mechanism of a liquid surface?

In the second place, it may be argued that even although it could be established theoretically that K should be the same for substances of the same molecular complexity, experiment indicates that this is not really the case.

Professor Ramsay's results show that K varies with the chemical nature of the substance. The extreme values for liquids the simple molecules of which are assumed to be unassociated differ by some 17 per cent. Moreover, there is also evidence that in the case of the same liquid K varies with the temperature. The data for the six liquids examined over wide temperature ranges by Professor Ramsay, especially those for ethylic acetate, seem to show that the theoretical straight curve for molecular surface energy cuts the observed curve generally in two points; the difference between theory and practice being, no doubt, small, but regular. If this be really the case, the slope of the curves, that is K, must vary with the temperature. But if K varies in this way, how are we to ascertain what value corresponds with an unassociated substance? In short, is it not rather premature in the present state of the question to definitely assess the weights of liquid molecules?

Professor Ramsay, in replying to Mr. Pickering, pointed out that the method of determining the molecular weights of liquids from variation of their surface energy could hardly be said to stand on a footing with those which involved osmotic pressure; in the one case, it is the behaviour of molecules widely separated from one another by molecules of a solvent which causes them to behave as gases, and to be practically independent of their mutual attraction; while in the other, it is this very attraction which makes it possible to determine the molecular weight of an undiluted liquid. It would be as unreasonable to expect the molecular weights of dissociating substances measured by these two methods to be identical as it would be to expect identity in the weights of the molecules of nitric peroxide measured at two widely different pressures.

He understood Mr. Pickering to refer to the comparative constancy of the molecular weights of such substances as butyric acid over considerable ranges of temperature. This is no doubt partly to be attributed to experimental error, but it no doubt implies only a small increase of dissociation with rise of temperature.

The number given for the multiple of H_2SO_4—32—might well be some units higher or lower.

In replying to Mr. Rodger, Professor Ramsay said that it was explicitly stated in the paper by Dr. Shields and himself in the *Philosophical Transactions*, that Eötvös's conclusion as regards the constancy of the temperature coefficient of molecular surface energy is true between wide ranges of temperature; and he would be very sorry if it were thought that credit were not due to Eötvös for his exceedingly ingenious work; especially for the brilliant conception of molecular surface. Exception was taken, first, to the method in which Eötvös deduced his theoretical conclusions, which are manifestly untenable; and also, probably owing to Eötvös's very imperfect means of securing high temperatures, to the equation from which the differential coefficient was derived. But Eötvös's conclusions, as well as his actual results, were quoted in full, and it is explicitly stated that Eötvös also made measurements with methyl and ethyl alcohols, and recognised that their approximate molecular weights might be calculated from their irregular behaviour; but his observations are not sufficient in number (*Trans.*, 1893, 1107). Conclusions drawn from the examination of more than sixty substances were surely more trustworthy than those drawn from eight, especially if some of the eight observations are heavily weighted with temperature errors.

Moreover, the credit of having first clearly pointed out that this "colligative" property is at present the only one by which the molecular weights of liquids could be determined is due to Ostwald, who devotes to it several paragraphs in his "Lehrbuch."

With reference to Mr. Rodger's criticism on the impropriety of drawing any conclusions regarding the molecular weight of liquids from their surface energy, based on the idea that Dr. Shields and he use the gas equation as a proof of the correctness of their method, this criticism was due to a misconception. The *analogy* was pointed out, but no attempt was made to construe it as a *proof*. That the simple gas equation is no longer valid when the liquid state is reached; that P is no longer equal to RT/V; such considerations cannot be urged to have any bearing on the fact that $\gamma = k(\tau - d)/v^{\frac{2}{3}}$. That a "push" given to a gas ceases, as the liquid state is approached, to obey a simple law cannot be urged as a reason why a "pull" given to a liquid should not be expressed by a simple equation.

It is true that k varies with the nature of the substance within certain limits, but so does R, the gaseous constant. And it is probable, indeed certain, that the configuration of the molecule should have a greater influence on the value of k than on the value of R, because in the liquid state the molecules are so much more closely packed. Experiments are in progress to discover the amount of variation of k, as chemical structure and composition vary.

As regards the non-constancy of k for any one liquid, that was fully alluded to in the original memoir in the *Philosophical Transactions*, and a formula is there given which approximately represents the variation from linearity at temperatures near, and also below, the critical point. Mr. Rodger's remarks, however, tended greatly to exaggerate this variation, which in no case exceeds 0·5 per cent, within reasonable distance of the critical point.

It was to be expected that in a preliminary investigation of the kind, certain discrepancies should be encountered, which will, doubtless, find their explanation later. But the examination of about sixty substances has shown that those which have normal gaseous densities possess a monomolecular formula in the liquid state; that the fatty acids, which exhibit a vapour density which implies association, also exhibit association when in the liquid state; and that other hydroxyl compounds, such as water and the alcohols, which the recent investigation of Dr. Sydney Young, with data furnished by himself alone, and by joint work with the speaker, have shown to exhibit abnormal behaviour near their critical points, only explicable on the theory of association, also exhibit molecular complexity in the liquid state. In the speaker's opinion, a strong case was made out by these surface energy experiments in favour of the justice of the hypothesis which had been advanced.

*99. "*Contributions to our Knowledge of the Aconite Alkaloids.* VIII. *On Picraconitine.*" By Wyndham R. Dunstan, M.A., F.R.S., and E. F. Harrison.

Through the kindness of Mr. F. B. Groves, of Weymouth, the authors have been enabled to examine specimens of salts of picraconitine, an amorphous alkaloid obtained by Mr. Groves, in the year 1874, from the roots of *Aconitum napellus*, the composition and properties of which were subsequently investigated by Dr. Wright (*Journ. Chem. Soc.*, 1877, 146; 1878, 332). Its composition was represented by the formula $C_{31}H_{45}NO_{10}$, that of aconitine being $C_{33}H_{43}NO_{12}$. It furnished crystalline salts and an amorphous aurichloride. When heated with alkalis, it underwent hydrolysis, yielding equimolecular proportions of benzoic acid and picraconine, a base closely

resembling aconine, the similar product from aconitine. Picraconitine was sparingly soluble in water, but readily in ether. Its salts have an intensely bitter taste, whence the names given to the substance, but they do not produce tingling of the tongue and lips which is so characteristic of aconitine. Mr. Groves had not previously obtained this alkaloid from other collections of the roots of this plant, and neither he nor Dr. Alder Wright was able to isolate it subsequently. It has, therefore, been suggested that it originated from the roots of some other species of aconite which were mixed in this collection with those of *A. napellus*. In the course of the present investigation of the alkaloids of *A. napellus*, no alkaloid having the composition of "picraconitine" has been obtained. Picraconitine, however, in many of its properties resembles the isomeride of aconitine, isaconitine. The fact that this isomeride is difficult to purify, except by adopting especial methods, suggested the view that "picraconitine" might be impure isaconitine. An examination of Mr. Groves's specimens of "picraconitine nitrate" and "picraconitine muriate" has confirmed this view. The base regenerated from these salts exhibited all the properties of isaconitine, and on converting it into the hydrochloride and purifying this salt, first by crystallisation from hot water and afterwards from a mixture of alcohol and ether, pure isaconitine hydrochloride, melting at 217°, was obtained. In order to complete the proof, the characteristic aurichlorisaconitine,—

$$C_{33}H_{44}(AuCl_2)NO_{12},$$

was prepared from the "picraconitine" salts. "Picraconitine" can therefore no longer be retained as the name for an alkaloid derived from *A. napellus*. The present investigation has shown that this plant contains, besides *aconitine* and the non-toxic *isaconitine*, and *aconine*, a very small quantity of an amorphous alkaloid yielding crystalline salts, which has been named *homisaconitine*, and generally a considerable quantity of a base which neither crystallises nor furnishes crystalline salts.

(To be continued).

NOTICES OF BOOKS.

Production of Chlorine and Hydrochloric Acid independently of the Leblanc Alkali Process. A Conspectus of the Methods Proposed. ("Darstellung von Chlor- und Salzsaüre, unalhängig von der Leblanc-soda Industrie. Eine Zusammenstellung der in Vorschlag gebrachten Verfahren.") By M. CARO. With 33 Figures. Berlin: R. Oppenheim. 1893.

IT is well known that in the struggle between the two great processes for the production of alkali—the Leblanc and that which is now known as the Solvay—a point of capital importance is the production of chlorine and of hydrochloric acid. If this end can be reached without the aid of the Leblanc process the doom of the latter is sealed. Hence a number of inventors have been, and still are, diligently engaged in the search for some method for the cheap production of chlorine and hydrochloric acid without decomposing sodium chloride by means of sulphuric acid. Dr. Caro has here supplied chemists with a very convenient conspectus of the processes proposed.

It has formed no part of his plan to enter upon a criticism of these new methods, since in most cases the main data required, results in actual practice, are entirely wanting.

The processes to be considered are arranged in five groups:—1. Methods for obtaining chlorine from the waste liquors of the ammonia-soda manufacture. 2. Processes for producing chlorine from the residues of the Leblanc-Weldon manufacture. 3. Methods for obtaining chlorine from the magnesium chloride of the Stassfurt potash works. 4. Processes for the direct production of chlorine from salt. A fifth and last group includes methods for the production of chlorine by electrolysis. This direction seems of late to attract the greatest attention. It does not appear that any of these processes shows a decided superiority over its rivals or is likely to be accepted in practice as the process of the future.

Remembrance of Eilhard Mitscherlich. (Erinnerung an Eilhard Mitscherlich"). 1794—1863. Berlin: E. S. Mittler and Son. 1894.

THIS interesting biographical treatise opens with a passage which cannot be entirely acquitted of Chauvinism. Says the author: "Towards the end of the Nineteenth Century Germany stands at the summit of all nations not merely by its warlike glory, but especially by the renown of the greatest scientific achievements." Comparisons, we know, are odious, but whilst fully and ungrudgingly recognising the scientific merit of Germany we must remember that she has not taken a predominating share in two great triumphs of the age—the periodic system and the doctrine of development.

The author, Alexander Mitscherlich, traces the career of his illustrious father as an inquirer in inorganic chemistry and crystallography, as an organic chemist, as a geologist, as a teacher, as an arranger of laboratories, and as an author. His official activity is next noticed. Here are included the opinions and decisions which he was required to furnish, and his activity in re-editing the Prussian Pharmacopœia. These labours left him, in the latter part of his life, little opportunity for research—a circumstance which the world must regret.

In his early life Mitscherlich does not seem to have shown any predilection for chemistry. On the contrary, his favourite subject was the study of Oriental languages, with a view to qualify himself for the consular service. He then turned to the study of medicine, that he might be able to maintain himself in Persia. But the necessary study of chemistry had for him such attractions that he made it the object of his life. After working in the laboratory of Berzelius, at Stockholm, he was appointed Professor of Chemistry to the University of Berlin.

Mitscherlich's relations with his colleagues were not always free from tension. With H. Rose, formerly his fellow student in the laboratory of Berzelius, and afterwards Professor of Analytical Chemistry at the University of Berlin, he was at first very intimate; but, from whatever cause, the two chemists ultimately became almost enemies. Of Liebig we find in this work only one mention, and that one not very complimentary. We read here that in the Giessen laboratory, where most of the chemists had worked under Liebig's direction, they were developed in a very one-sided direction. But those who wish to understand the mutual relations of the chemists of the earlier half of the present century will do well to compare the present volume with the correspondence of Berzelius and Woehler. A more comprehensive account of the life and researches of Mitscherlich is in course of preparation.

Catalogue of Standard Second-hand and New Books, English and Foreign, on Chemistry and the Allied Sciences, Technology, Physical and Electrical Science, Metallurgy, Mineralogy, Brewing, Dyeing, Manufactures, Agriculture, &c. By WILLIAM F. CLAY, Edinburgh.

WE have repeatedly had occasion to notice the catalogues of scientific books issued periodically by Mr. W. F. Clay, and to call attention to the many rare and important works which he offers at very reasonable prices. From the present issue of the catalogue we see that Mr. Clay's activity is still successful. Students in search of some desideratum reputed as being out of print may often obtain the work they are seeking on applying to the Edinburgh University Book Warehouse.

University College of Wales. Prospectus of the Agricultural Department; and Report on Experimental Manuring. By J. Alan Murray, B.Sc., Aberystwith.

The foundation of agriculture, as of every other science, is in observation and experiment. Until Sir John Bennet Lawes started his now famous experimental farm at Rothamsted, about fifty years ago, this does not seem to have been realised. His valuable results have prompted the Agricultural Department of this College to endeavour to obtain more exact knowledge of the best conditions under which agriculture can be carried on in their own particular districts. To this end they sought the co-operation of local farmers and landed proprietors, and were warmly supported by them.

During the first year there were naturally many difficulties and delays, so that only two actual experiments on a large scale were started, and only one up to the present, viz., on manuring grass land, has been actually finished. All the details and particulars of this experiment are here given in a number of tables, and the author arrives at the conclusion that the most profitable manure for hay crops is a mixture of 1 cwt. of superphosphate, mixed with 2 cwts. of nitrate of soda per acre, while the profit steadily decreases as the proportion of phosphate is increased beyond that limit.

The Agricultural Department of the College is in receipt of a grant from the Board of Agriculture, as well as from some half-dozen County Councils, of which three have further given sums of £100, £50, and £25 for scholarships, besides three extra sums for advanced dairy work.

The course extends over a period of two years, and embraces all the ordinary subjects of modern science-teaching, special attention being paid to those subjects having a direct bearing on agriculture, and finishes with the inevitable examination.

We must, however, confess to some surprise that special importance is attached to the fact that students have the advantage of a professor of Welsh, in order that they may learn that language. Without wishing to put any slight upon "gallant little Wales," we must express our opinion that Welsh is a language which is of no practical use outside its own country, and is, moreover, extremely difficult to learn; and as all the Board Schools in Wales, as in the rest of Great Britain, are conducted entirely in English, it is highly probable that, as a language, Welsh will quickly die out.

Besides the ordinary terms, there is an extra Summer Course, held in August, for the benefit of those whose ordinary avocations prevent them attending the regular College Courses of the Session.

CORRESPONDENCE.

CHEMISTRY AT THE CONJOINT BOARD.

To the Editor of the Chemical News.

Sir,—On the 15th December, 1893, a certain medical student presented himself at the Terminal Examination of the Chemistry Classes in this College. He knew nothing at all. I gave him 5 per cent of marks *pro formâ*. As an example of his answers, this is what he wrote about ammonia: "Ammonia is prepared by heating in a glass retort a mixture of potassium nitrate and a hydrogen acid,—

$$KNO_3+3HCl=NH_3+KClO_3+Cl_2.$$

The gas is given off and collected under warm water, as it is soluble in cold. Ammonia has an intensely penetrating odour. Reaction neutral." This student appeared before the Conjoint Board in London on January 2nd—that is, a fortnight later—and passed!

As you are aware, the Colleges of Physicians and Surgeons have jointly issued a syllabus of subjects in chemistry which is supposed to represent the range of the examination in this department of science, instruction in which is to be given in their first year to students in the medical schools. I have reason to believe that the case of which I have given you an account is by no means an isolated or accidental one. What are the teachers of chemistry in the medical schools to understand? Is the syllabus issued by the Colleges intended to impose upon the public the idea that all medical students are required to learn the rudiments of chemistry, while at the same time private instructions have been issued to the Board that the examination in chemistry is to be a farce? Or are we to believe that the examiners in chemistry are systematically neglecting their obvious duty? I cannot perceive a way of escape from these alternatives.

I will not now criticise the syllabus, neither do I think it necessary at this moment to enter upon the question of the utility of chemistry as a subject of instruction in the medical curriculum. The question which concerns me and all the other professors of chemistry connected with the medical schools of England, is simply this: Do the Royal College of Physicians and the Royal College of Surgeons of England in the exercise of that monopoly with which they have been entrusted, practise systematic deceit towards the public, or do they not? If not, let them instruct their examiners to do their duty, and reject all unqualified candidates, in no matter what subject, so long as that subject is a recognised element in the curriculum. And as to "standard," I imagine that the greatest advocate of leniency in examinations will hardly maintain that the youth who thinks ammonia is a neutral substance possesses a stock of chemical knowledge adequate to any practical purpose whatever.—I am, &c.,

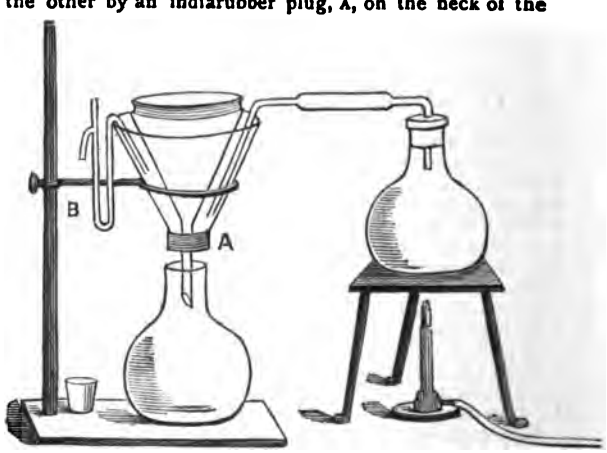
William A. Tilden.

Queen's Faculty of Medicine,
The Mason College, Birmingham,
January 29, 1894.

HOT-WATER FUNNEL.

To the Editor of the Chemical News.

Sir,—I have lately constructed a simple form of hot-water funnel which, I think, is better in some respects than the ordinary copper-jacketted funnel usually employed for filtering liquids which require to be kept hot during the process. It consists of two glass funnels fitted one inside the other by an indiarubber plug, A, on the neck of the



inner funnel, around which the outer funnel fits as a collar. The top of the inner funnel projects somewhat in order that the filtering liquid may be conveniently covered. The interspace contains water, which is kept hot by blowing steam into it, and the excess of water thus formed is

carried away by a constant level syphon, B; a strip of wet tape hanging over the edge of the outer funnel answers the same purpose.

The chief virtue of this kind of hot water funnel lies in the fact that it can be constructed in a few minutes out of ordinary laboratory apparatus at a very small cost; but it has a second advantage, for by employing steam to maintain the temperature instead of the naked flame generally used with the copper-jacketted funnels, all risk of inflammable vapours from spirituous and other liquids becoming ignited is avoided.

I think a hot-water funnel of this kind has not been described before. I therefore hope that this account may be of practical interest to some of your readers.—I am, &c.,

CHARLES R. BECK.

Clifton College, Bristol,
January 22, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 3, January 15, 1894.

Obituary.—Official notice was given of the death of Prof. P. J. Van Beneden, of the University of Louvain, a Foreign Associate of the Academy, who died on the 8th inst. in the 85th year of his age.

Studies on the Formation of Carbonic Acid and the Absorption of Oxygen by the Detached Leaves of Plants. Experiments made at the Ordinary Temperature, with the Co-operation of Biological Actions.—M. Berthelot and G. André.—The oxygen fixed upon carbon in the formation of carbonic acid is almost entirely derived from the oxygen of the atmosphere to the exclusion of that of the plant. Therefore the carbonic acid has not been produced by anærobic ferments, contrary to what has been supposed in alcoholic fermentation. It will be observed that the ratio in volume of the carbonic acid exhaled compared to the oxygen fixed has been approximately equal to unity exactly as in the respiratory phenomena of animals.

A Method intended for Studying the Exchanges of Gases between Living Beings and the Surrounding Atmosphere.—M. Berthelot.—The leaves are to be placed in a flat-bottomed capsule in a very thin layer over a wide receptacle filled with concentrated sulphuric acid, the whole under a large bell holding about 4½ litres and adjusted on a plate of ground glass. After some days we introduce slowly, bubble after bubble, by aspiration a current of pure dry air at about the centre of the bell and lasting four to five hours. The removal of the gases escaping takes place at the upper part. We pass in a volume of air (determined by the volume of the water escaped from the aspirator) equal to the volume of the air contained in the bell, and determine gravimetrically by means of potassa the carbonic acid contained in the air withdrawn from the bell. This operation is repeated once or twice weekly until the regular decrease of the weight of the carbonic acid indicated that there was no further production of this gas. Its development is stopped by the effect of the desiccation, which suspends all vital reaction. We may thus study in a continuous manner the production of carbonic acid by the plant.

Is there Oxygen in the Atmosphere of the Sun?—Prof. Arthur Schuster.—With reference to M. Duner's communication on this subject (*Comptes Rendus*, Dec. 26), the author points out that in a letter published in *Nature*, Dec. 20, 1877, he remarked that one of the spectra of oxygen seems, in fact, to be found among the Fraunhofer lines. In his researches on the spectrum of oxygen he has shown that we must distinguish two-line spectra, one of which appears at low temperatures and corresponds to the band spectrum of nitrogen and other gases. We generally ascribe the fluted band spectra to more complex molecules, and for this reason he names this spectrum the spectrum of compound lines. It is remarkable that among the lines which often appear in the spectrum of the chromosphere Young gives the wave-lengths 5435·4 and 5329·1, and in fact if the solar atmosphere contains oxygen we may expect to find it in the chromosphere.

Combination of Hydrogen and Selenium in a Space Unequally Heated.—H. Péladon.—If no point of the tube has a temperature below 270° the gaseous mixture acquires the same composition as if the entire tube had been brought to the temperature of its coldest point. The excess of selenium after the experiment occupies the coldest end of the tube. If the hottest part of the tube has a temperature above 270° and the coldest point is below 270°, the composition of the gaseous mixture is independent of the temperatures of the two extremities of the tube. If the temperature of the hottest extremity is below 270° the gaseous mixture has the same composition as if the tube had been entirely raised to the temperature of the hottest part of the tube.

Ceric Bichromate and the Separation of Cerium from Lanthanum and Didymium.—G. Bricourt.—(See p. 54).

Researches on the Desiccation of Starch.—MM. Bloch.—The authors find that temperatures of 100° or 110° do not suffice, but that temperatures of 155° or even 160° are necessary for the complete desiccation.

Liquid of Albuminous Periostitis.—L. Hugounenq.—The author assigns to this secretion the following composition:—

Water	91·61
Fixed matter	8·39
Nucleo-albumen	0·87
Serine	5·61
Succinic acid, urea, fat, extractive matter	0·98
Mineral salts	0·93

Influence of Atmospheric Agents, especially Light and Cold, upon the Pyocyanic Bacillus.—MM. D'Arsonval and Charrin.—The bactericide influence of light is not distinct when we direct upon the bacteria either the solar spectrum or that of the arc. Microbia support low temperatures very well. Some species have been observed in ice, snow, hail, &c. This resistance explains winter epidemics. The pyocyanic bacillus under the influence of cold promptly loses its pigmentary properties; but for its destruction we require temperatures of −40° to −60°.

MISCELLANEOUS.

Antiseptic Value of Ozone.—J. de Christmas.—The author's experiments show that ozone added to air in the proportion of 0·1 per cent (volume) possesses antiseptic properties, as a development of the spores of pathogenic microbia ceases to occur on the surface of objects exposed to this gaseous mixture. But as soon as the proportion of ozone falls below 0·1 per cent by volume all antiseptic action disappears. Hence ozone must be rejected as unsuited for the practical disinfection of our houses and hospitals. On the one hand, the practical difficulties presented by the production of ozone in the necessary quantity have not been overcome. On the other hand, the air becomes unfit for respiration long before it is saturated with ozone to the degree required. Hence all appliances and "ozonisers" recommended for disinfection depend upon an erroneous assumption.—*Annales de l'Inst. Pasteur* and *Chemiker Zeitung*.

Definition of Diamond.—Dr. E. O. von Lippmann, writing in the *Chemiker Zeitung*, quotes a dictum of the physiophilosophers that diamond is quartz which has arrived at self-consciousness! The author of this strange dictum is supposed to have been Steffens. It has been parodied by an eminent geologist as "quartz is diamond which has become insane!"

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Medical, 8.30.
— Society of Arts, 8. (Cantor Lectures). "The Detection and Measurement of Inflammable Gas and Vapour in the Air," by Frank Clowes, D.Sc.
— Society of Chemical Industry, 8. "Note on an Interesting Explosion caused by Sodium Peroxide," by Dr. A. Dupré. "Theory of Dyeing—Part I. Ingrain Colours," by P. W. Dreaper.
TUESDAY, 6th.—Royal Institution, 3. "Locomotion and Fixation in Plants and Animals," by Prof. Charles Stewart, Pres.L.S.
— Institute of Civil Engineers. 8.
— Pathological, 8.30.
WEDNESDAY, 7th.—Society of Arts, 8. "Automatic Balance of Reciprocating Machinery, and Prevention of Vibration," by W. Worby Beaumont.
— Geological, 8.
THURSDAY, 8th.—Royal, 4 30.
— Royal Society Club, 6.30.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "The Past and Future of Mountain Exploration," by W. Martin Conway, M.A., F.R.G.S.
— Society of Arts, 4.30. "Telegraphic Communication between England and India—its Present Condition and Future Development," by E. O. Walker, C.I.E., M.I.E.E.
FRIDAY, 9th.—Royal Institution, 9. "Fortuitous Variation in Animals," by Prof. W. F. R. Weldon, F.R.S.
— Astronomical, 3. (Anniversary).
— Physical, 5. (Annual General Meeting). "On the Viscosity of Liquids," by O. G. Jones.
SATURDAY, 10th.—Royal Institution, 3. "Light, with special reference to the Optical Discoveries of Newton," by the Right Hon. Lord Rayleigh, F.R.S.

FLETCHER'S
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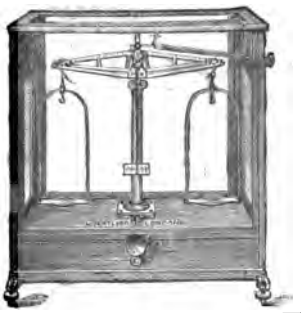

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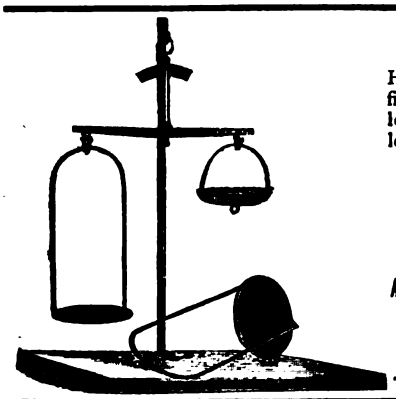

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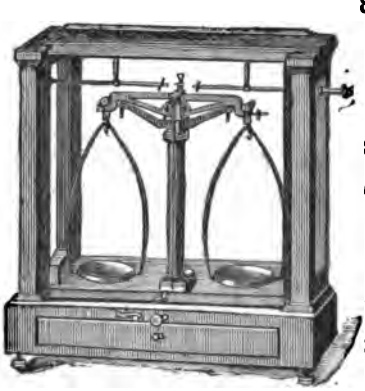

FIG. 3a.

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ON THE

PRECIPITATION OF BARIUM SULPHATE IN PRESENCE OF SILICA, AND THE DECOMPOSING ACTION OF HYDROFLUORIC ACID ON THE FORMER.

By J. F. SLEEPER.

A STATEMENT having been made not long ago that barium sulphate containing SiO_2 as an impurity could be freed therefrom by simple evaporation with HF, and it, besides being the commonly received opinion amongst many chemists that SiO_2 is co-precipitated with $BaSO_4$ in the fusion process for S estimation, unless the filtrate from the lixiviated "melt" is evaporated to dryness with HCl before addition of $BaCl_2$, I was requested by Mr. Lucius Pitkin, of 138, Pearl St., New York, to investigate the matter, and endeavour to prove the verity or fallacy of the assertion.

The first step was to prepare pure sulphate of soda solutions containing exactly equal quantities of pure H_2SO_4. Sulphuric acid of the best obtainable quality was mixed with water in a 500 c.c. flask to a convenient degree of dilution, cooled, water added to the mark, and the flask well agitated. Four portions of this were drawn out successively with a 50 c.c. pipette, each being delivered into a 700 c.c. beaker, and the instrument thoroughly washed out with water into the beaker receiving the fluid after each discharge.

It will be seen that this method of measuring, carefully performed, admitted of very delicate comparative work.

Each of these four portions were then carefully alkalised with equal volumes of pure Na_2CO_3 solution.

I then prepared a solution of sodium silicate in order to add a known amount of silica in a soluble form to two of these. Some colourless rock crystal was finely comminuted and fused with pure Na_2CO_3 in platina over a blast lamp, cooled, the mass boiled with distilled water and filtered, then diluted to 200 c.c. and well agitated.

50 c.c. of this silicate solution was added to each of two of the alkaline sulphate fluids previously mentioned, the remaining two being left unchanged. 50 c.c. more of the silicate solution was delivered into a fifth beaker, and run as a "blank test" for sulphates. The remaining 50 c.c. was submitted to analysis to determine its content of SiO_2—supposed to range between 40—50 m.grms. (and thus on a 1 grm. basis represent 4—5 per cent of that acid rendered soluble from a pyrites). It was acidulated with HCl, the CO_2 boiled out, fluid evaporated to dryness, dried some time, moistened with HCl, taken up with H_2O, and filtered; ashless filter well washed, ignited in a small crucible, and blasted over a powerful lamp, then weighed.

Cru. + SiO_2	16·5312 grm.
Cru.	16·4867 ,,
SiO_2	0·0445 ,,

All being ready the comparative experiments were begun:—

All five of the solutions were diluted to the same bulk (about 400 c.c.), about 15 c.c. of HCl added to each, and all boiled to expel CO_2. No separation of silica (even manifested by turbidity) was evident in any of the fluids, though they were carefully observed at various angles of reflection. NH_4HO was then added to each until just alkaline, then 4 c.c. of HCl discharged into each, and all five well stirred. No separation of silica.

A solution of freshly-prepared pure $BaCl_2$ in distilled water (1 : 10) was filtered, and let fall drop by drop from an alkalimeter into the nearly boiling liquids, constant brisk stirring being maintained until 30 c.c. of it had thus been added to each.

The precipitated solutions were allowed to stand over night. Next morning they were filtered off, the precipitates being carefully retained in the beakers, digested with 1 c.c. of HCl and 40 c.c. of hot water + a few drops of $BaCl_2$ solution for fifteen minutes on a water-bath, and then brought upon the ashless filters. Each filter was washed six times with cold water. The precipitate dried and ignited in the same platinum dish successively over the same Bunsen flame. (See Table below).

The same dish and burner was used in order to preserve the same conditions during ignition, cooling, and weighing, and as it was well polished after each precipitate was removed from it, it decreased more or less in weight each time. $CaCl_2$ desiccators were employed.

It will be seen that no silica was precipitated in either case with the $BaSO_4$.

IV. was evaporated with four drops of H_2SO_4 and 8 or 10 c.c. of H_2O; it exhibited no increase of weight.

It now remained to determine whether, supposing it possible by some other process to get SiO_2 co-precipitated with $BaSO_4$, a simple evaporation with HF alone would remove the former, leaving the $BaSO_4$ unchanged.

Pure $BaSO_4$ was therefore thus prepared:—

Five c.c. of C.P. sulphuric acid was largely diluted with distilled water, 5 c.c. of conc. HCl added, the whole heated to boiling in a large beaker, and precipitated, drop by drop, with a 1 : 10 solution of $BaCl_2$ (freshly prepared and filtered); the precipitate was collected on ashless filters and washed thoroughly with cold water, dried in an air-bath, the *loose* precipitate removed from the filter and ignited in large platina dishes nearly to redness. The well mixed powder was bottled.

Upon this the following experiments were tried:—(See Table next column).

These experiments show conclusively that mere evaporation with HF is sufficient to decompose $BaSO_4$, that the loss increases with the augmentation of the volume of acid used in each evaporation, and that it is probably

Results of Experiments.

Pure sulphate.	I. Pure sulphate.	II. Pure sulphate.	III. Sulphate + silicate.	IV. Sulphate + silicate.	Blank test silicate, Na_2CO_3, HCl, or NH_4HO.
$BaSO_4$ + dish ignited to a constant weight	34·8670	34·8638	34·8592	34·8569	
	34·8651	34·8634	34·8589	34·8568	A mere
	34·8649	34·8634	34·8589	34·8568	trace,
Weight of dish	32·7277	32·7266	32·7235	32·7221	not
$BaSO_4$	2·1372	2·1368	2·1354	2·1347	weighable.

	I.	II.	III.
Weight of Pt dish	49·3468	49·3492	32·7279
$BaSO_4$ taken + dish	51·5031	52·2617	34·7293
Control weighings after ignition	51·4995	52·2617	34·7271
	51·4994	—	34·7271
Evaporation with HF (Baker and Adamson's acid in ceresine bottles) .. (1)	51·4925	52·2591	34·7201
Ditto .. .. (2)	51·4763	52·2522	—
Ditto .. .. (3)	51·4692	52·2425	—
Ditto .. .. (4)	51·4509	52·2234	—
Ditto, acid diminished (5)	51·4490	—	—
Ditto, acid increased .. (6)	51·4268	—	—
Ditto, „ „ .. (7)	51·4017	—	—

capable of prolongation until all the $BaSO_4$ is decomposed. The residue left in the case of I. was digested with very dilute HCl and H_2O, filtered, and H_2SO_4 added to the filtrate; a heavy precipitate of $BaSO_4$ fell immediately. On drying the filter and contents and weighing the ignited residue the following result was obtained:—

Dish + residue ..	51·0554
Dish	49·3457
Residue	1·7097

Hence 0·4429 grm. of substance dissolved by a single dil. HCl treatment.

The residue was still capable of yielding soluble matter to dilute HCl.

I next ascertained what effect would be produced by evaporation with $HF+H_2SO_4$:—

Weight of dish	55·9189	32·7279
„ „ $+BaSO_4$..	57·9363	34·7271
Ignition to constant weight	57·9328	34·7248
	57·9328	34·7246
Evaporation with 2 drops H_2SO_4 and usual HF ..	57·9150	34·7181
Ditto, 6 drops and HF ..	57·9335	34·7251

The above results indicate that *a very small* quantity of H_2SO_4 does not prevent decomposition, larger quantities do.

I concluded the experiments by examining the effect of H_2SO_4 on the $BaSO_4$ used in the investigation, in order to ascertain whether any Ba salts were present, and by evaporating down a volume of HF equal to that employed in the treatments of the weighed portions of $BaSO_4$.

	I.	II.
$BaSO_4$ + dish to constant weight	34·7246	57·9363
	34·7244	57·9328
Dish	32·7279	55·9189
Moistened with 8—10 drops H_2SO_4 and 5 c.c. of H_2O	34·7248	57·9333
Repeated	34·7246	57·9335

Trial of the HF.

Dish	49·3450
After evaporation and ignition	49·3461
Residue (chiefly iron oxide) ..	0·0011

No barium salts, therefore, contaminated my sulphate, and the hydrofluoric acid was very pure.

City and Guilds of London Institute. — The Executive Committee of the City and Guilds of London Institute have changed the name of the Guilds Central Institution, in Exhibition Road, to the Guilds Central Technical College.

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

SECOND PAPER: THE ANALYSIS OF BARIC CHLORIDE.

By THEODORE WILLIAM RICHARDS.

Introduction.

DURING the time occupied by the recent investigation of baric bromide (*Proc. Amer. Acad. Arts Sci.*, xxviii., 1; *Zeit. Anorg. Chem.*, iii., 441; iv., 160), similar analyses of baric chloride were being made. The problem involved was far more complicated than the one already published, because of the solubility of argentic chloride in water; hence the present paper, which might well have come first, was necessarily postponed. The results of the continued investigation confirmed the high value of the atomic weight of barium, 137·43, obtained from the results of the investigatigation of baric bromide.

The balance and weights, and all the precautions relative to the weighings, have been already described in detail (*Ibid.*, xxvi., 242; also xxviii., 5). The remarks made before about the constancy of the weights, and the various comparisons with the Washington standard, naturally apply with equal force to the present work. At the close of the two years' investigation the weights were again compared, and were found to have remained surprisingly constant in relative value.

The following atomic weights of various elements entering into the present research will be assumed throughout the paper:—

Oxygen	= 16·000	Hydrogen	= 1·0075
Bromine	= 79·955	Silver	= 107·930
Chlorine	= 35·456	Sulphur	= 32·065

Properties of Baric Chloride.

The properties of baric chloride are so familiar as to need little further description.† The colourless flat tables of the rhombic system contain, as is very well known, two molecules of water together with the usual slight excess. Half of this water is given off at 60—65° (Lescœur, *Compt. Rend.*, civ., 1511), and the rest at somewhat higher temperatures. All the water is regained at ordinary temperatures in ordinary moist air. According to Filhol (Graham Otto (Michaelis), *loc. cit.*) the crystals possess a specific gravity of 2·66, while according to Joule and Playfair (*Chem. Soc. Mem.*, ii., 401; iii., 57, 199), Schiff (*Annalen*, cviii., 21), and Schroeder (*Jahresberichte*, 1879, p. 31) they possess a specific gravity of about 3·05. This great discrepancy is too serious to neglect, hence a re-determination was made.

The apparatus for the determination of the specific gravity was similar to that already described (*Proc. Amer. Acad. Arts. Sci.*, xxviii., 14), and toluol was again used as the liquid to be displaced. 5·701 grms. (in air) of powdered crystallised baric chloride were found to displace 1·5864 grms. of toluol at 24°, or 1·8408 grms. of water at 4°. Hence the specific gravity sought is 3·097. The reason for at least a part of the discrepancy is undoubtedly to be found in the enclosure of varying amounts of mother-liquor in the crystals.

The specific gravity of anhydrous baric chloride has been much more definitely determined. According to Quincke (Graham Otto (Michaelis), iii., 659), the value of this constant is 3·851 at 0°; according to Favre and Volson (*Ibid.*), it is 3·844 at 17°; and according to Schroeder (*Ber. d. Deutsch. Chem. Gesell.*, 1878, 2131), it is 3·879 at 4°. Although without doubt the mean of these values would have served the present purpose, a new determination was made, as much to check the previous

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences.*

† See Graham Otto (Michaelis), III., 658; also "Watts' Dictionary" (Muir), I., 441, &c.

determinations in the present research as to serve for the basis of reduction to vacuum.

4·8620 grms. (in air) of baric chloride which had been dried to constant weight at 220° were found to occupy the same volume at 24° as 1·2608 grms. of water reduced to 4°. Hence the specific gravity of baric chloride under these conditions is 3·856, a value which agrees essentially with those given above.

Here, as in the case of baric bromide, the question whether the water of crystallisation is absolutely expelled at a red heat is one of the greatest importance. All early experiments have assumed that this is the case, without attempting to disprove the contrary assumption. The first stumbling-block in the way of the careful investigation of the problem is the decomposition of baric chloride in the air at high temperatures. Marignac's statement that the salt may be ignited at a dull red heat without the loss of a trace of chlorine (*Liebig's Annalen*, lxviii., 215; cvi., 165) has not been confirmed by the present experience. As a matter of fact, baric chloride loses almost as much halogen as the bromide, upon gentle ignition in the air (Schultze, *Journ. f. Prakt. Chem.*, [2], xxi., 407). Hence in order to determine the true weight of baric chloride present in all those cases where the salt was ignited in this way, it was necessary to determine the amount of baric hydroxide and baric carbonate existing in the solution of the ignited salt. Pure boiled water which had been prepared solely in platinum was used for making this solution, and phenolphthalein and methyl-orange were used as indicators. Of course, the loss of 0·00355 grm. of chlorine would correspond to a correction of +0·00055 grm. to the weight of the baric chloride if the alkaline earth were in the form of carbonate, +0·00185 grm. if it were in the form of hydroxide, or +0·00275 grm. if it were in the form of oxide. Since it is somewhat uncertain whether the portion which is determined by phenolphthalein really exists when dry in the form of hydroxide, and not in the form of oxide, the mean of the last two figures, 0·0023 grm., was adopted in the work which follows. In the case of baric bromide, this correction was calculated for the hydroxide. The corrections are in any case so very small that the possible error introduced by either method of procedure is quite unimportant. Another possible error of about the same magnitude is to be found in the fact that pure baric carbonate is not wholly without influence on phenolphthalein.

In order to observe the behaviour of baric chloride under gradually increasing heat, specimens of very pure material were heated at many different temperatures by means of a Berzelius spirit-lamp, and finally raised to redness. The residues were then dissolved in water and the alkalimetric corrections were determined and applied in the manner which has just been described. Below are given the experimental data:—

1. 3·17+ grms. of pure baric chloride which had been dried to constant weight (for twelve hours) at 260°± lost 0·27 m.grm. on heating to somewhat over 300°, 0·18 m.grm. more on heating to about 450°, and yet 0·30 m.grm. upon ignition at a medium red heat. To neutralise the baric hydroxide found upon dissolving the salt, about 0·4 c.c. of the standard solution of hydrochloric acid was required. Since a c.c. of this solution corresponded to a m.grm. of silver, it is evident that the correction to be added to the weight of baric chloride amounted to 0·09 m.grm.

2. About 3 grms. of baric chloride dried at 400° lost no weight on heating to redness. The alkalimetric correction was +0·12 m·grm.

3. About 5·0 grms. of baric chloride dried at 400° lost 0·17 m.grm. on heating to dull redness. The alkalimetric correction to be added to the weight of the baric chloride amounted to 0·12 m.grm.

4. 5·46 grms. of baric chloride dried at 250° lost 0·66 m.grm. on heating to dull redness, 0·22 m.grm. of this loss being accounted for by the alkalimetric correction.

5. A repetition of Experiment 4 showed a loss of 2·0 m.grms. between 250° and dull redness, only 0·10 m.grm. of this amount corresponding to the alkaline earth found.

6. About 4·0 grms. lost 1·20 m.grms. between 300° and dull redness, the alkalimetric correction being only 0·06 m.grm.

7. 2 61 grms. of baric chloride dried at 300° lost 0·40 m.grm. upon being ignited to a bright red heat in a stream of nitrogen. 0·15 m.grm. of this loss was due to substitution of oxygen for chlorine.

8. 6·37 grms. of baric chloride which had been dried at 200° lost 1·75 m.grms. of water upon being heated to 300°±, and 1·30 m.grms. more upon being partly fused at a bright red heat in a stream of nitrogen. The alkalimetric correction was +0·74 m.grm. (Reference will be made to this later on).

9. 3·6 grms. of baric chloride dried at 300° lost 0·32 m.grm. upon being heated to dull redness, only 0·04 m.grm. being due to loss of chlorine.

10. 3·11 grms. of baric chloride which had been prepared by drying large clear crystals at 160° lost 0·70 m.grm. on heating to dull redness. The alkalimetric correction was 0·29 m.grm.

11. 2·65 grms. heated to dull redness lost 0·17 m.grm. upon being further heated to bright redness. The alkalimetric correction was +0·25 m grm.

12. 1·5 grms. heated at 250° lost 1·0 m.grm. on fusion in a stream of dry, pure hydrochloric acid gas. No trace of alkali or acid was found in the concentrated solution of the residue, but the addition of 0·10 c.c. of hundredth normal hydrochloric acid made the neutral solution perceptibly acid to methyl-orange.

13. 5·36 grms. dried at dull redness lost no weight on fusion in hydrochloric acid at bright redness. The residue was wholly neutral.

14. 3·92 grms. dried at dull redness lost 0·13 m.grm. on fusion in hydrochloric acid. The heat was so great that the crucible was attacked.

15. 4·28 grms. of baric chloride dried a dull redness *gained* 0·23 m.grm. on partial fusion in hydrochloric acid. This specimen, as well as the previous one, was absolutely neutral.

The accompanying table contains a summary of all the experiments, reduced to a common basis. Thus the column headed "Dull redness" shows that on the average baric chloride ignited at about 500° or 600° loses three parts in one hundred thousand of its weight. The true weight of the baric chloride was computed in each case by adding the alkalimetric correction to the last weight taken; and then the percentage of excess or deficiency in weight was computed for each temperature and tabulated in its appropriate place.

The variations noticeable in the amounts of water retained at the lower temperatures are probably in great part due to the varying hygroscopic condition of the atmosphere at the time of drying, as well as to inaccuracies in the temperatures recorded.

There are necessarily three standards for determining the true weights of baric chloride forming the basis of the table above: one involves the weight of the salt ignited at dull redness plus the alkalimetric correction (Experiments 1, 2, 3, 4, 5, 6, 9, and 10); another involves the weight of the salt ignited at bright redness plus the same correction (Experiments 7, 8, and 11); and the third involves the weight of the salt fused in hydrochloric acid, without any correction (Experiments 12, 13, 14, and 15). A comparison of the results of Experiments 11, 13, and 15 with all the earlier experiments is sufficient to show that the three standards are very nearly, if not quite, identical; in other words, that baric chloride which has been dried at dull redness, or even at 400°, does not lose an essential amount of water upon being heated nearly to 900°. Nevertheless, below 400°—which is about the point at which the salt begins to show signs of partial decomposition—very noticeable amounts of water appear to be held by the so-called anhydrous salt.

Action of Heat on Baric Chloride.

No. of Exp.	About 200°. Per cent.	About 250°. Per cent.	About 300°. Per cent.	About 400°. Per cent.	Dull redness. Per cent.	Bright redness. Per cent.	Fused in HCl. Per cent.
1.		+0·021	+0·012	+0·006	−0·003		
2.				−0·004	−0·004		
3.				+0·001	−0·002		
4.		+0·009			−0·004		
5.		+0·038			−0·002		
6.			+0·029		−0·002		
7.			+0·014			−0·006	
8.	+0·036		+0·009			−0·011	
9.			+0·008		−0·001		
10.	+0·013				−0·009		
11.					−0·003	−0·010	
12.	+0·066						0·000
13.					0·000		0·000
14.					+0·003		0·000
15.					−0·005		0·000
Average	+0·038	+0·023	+0·014	+0·001	−0·003	−0·009	0·000

The conclusion regarding the expulsion of water from the baric chloride is so important that it seemed desirable to prove it in another way. Hence two determinations of the water of crystallisation of perfectly homogeneous powdered pure baric chloride were made by two distinct methods:—

16. In the first case 3·10784 grms. (in vacuum) of the powdered crystals were dried at a medium red heat, by means of a spirit-lamp, to the constant weight of 2·64851 grms. (in vacuum) and cooled in a vacuum over phosphoric anhydride. The solution of this salt required 1·00 c.c. of standard hydrochloric acid (of which the c.c. corresponded to a m.grm. of silver) to render it neutral to phenolphthalein, and 0·85 c.c. more to reach the neutral point with regard to methyl-orange. Hence the alkalimetric correction is found to be 0·00025 grm., and after adding this weight to the observed weight of the dried salt, the true per cent of water present in the original crystals is found to be 14·7717.

17. Again, 5·02356 grms. (in vacuum) of the same sample were dried in a platinum crucible at about 400° by means of the spirit-lamp, and then fused in a stream of pure dry hydrochloric acid gas in a double crucible. The constant outflow of hydrochloric acid was sufficient to prevent the absorption of sulphuric acid from the products of the combustion of the illuminating gas, hence it was possible to use this source of heat. Indeed, the highest temperature obtainable by means of a powerful Bunsen burner is required to fuse the salt. After fusion, the salt was found to weigh 4·28148 grms. (in vacuum), having lost 14·7720 per cent.

These results (14·7717 and 14·7720) agree within the limit of the probable experimental error; therefore very satisfactory confirmation is given to the conclusion arrived at before. Hence baric chloride is a compound of sufficient definiteness to form a very satisfactory basis for the determination of the atomic weight of barium.

The other properties of the salt—its solubility in water and insolubility in alcohol, the specific gravity of its solution, and so forth—have been studied by Gay Lussac, Gerlach, Karsten, Kopp, Mulder, and many others, and further remark upon them is unnecessary here.

(To be continued).

Condensation of Isovalerianic Aldehyd with Ordinary Acetone.—Ph. Barbier and L. Bourcault.—The substance which the authors have obtained (isoamylidenacetone) is distinctly different from the methylheptonone of Wallach.—*Comptes Rendus*, cxviii., No. 4.

NOTES ON THE OXIDES CONTAINED IN CERITE, SAMARSKITE, GADOLINITE, AND FERGUSONITE.*

By WOLCOTT GIBBS, M.D.,
Rumford Professor (Emeritus) in Harvard University.

(Concluded from p. 57.)

RECENT determinations of the molecular masses of the cobaltamines have shown that the chlorides, for example, of roseocobalt and luteocobalt are represented respectively by the formulæ $Co(NH_3)_5Cl_3$ and $Co(NH_3)_6Cl_3$. I have kept the old formulæ only to permit an easy comparison with those given by Wing, and the matter is not one of consequence in this place. It may also be remarked that, as cerium is at present the only one of the group which forms a well-defined oxide higher that R_2O_3, the two formulæ II. and IV. cannot be generalised by substituting the symbols of other elements for that of cerium. I have endeavoured, however, to prepare such compounds by adding a solution of $Lc_2(SO_4)_3$ to one containing the sulphates of oxides other than the cerite oxides, and then adding some oxidising agent, as, for instance, potassic permanganate, chlorine, or bromine. No decisive results were obtained. It is at least probable that all the earths the sulphates of which in cold solutions give only slightly soluble double sulphates with potassic and sodic sulphates will also give insoluble double sulphates with sulphate of luteocobalt. These earths are, so far as now known, Ce_2O_3, La_2O_3, Nd_2O_3, Ps_2O_3, Sm_2O_3, Sc_2O_3, while the following give soluble double sulphates: Er_2O_3, Y_2O_3, Yb_2O_3, and Tb_2O_3. The four cerite oxides cited are not the only ones which give insoluble crystalline precipitates with sulphate of luteocobalt in the cold, but I am not at present able to give more accurate information on this point. On the other hand, we meet in the case of luteocobalt sulphate with some of the relations which present themselves when the alkaline sulphates are employed. Thus sulphate of yttria is not precipitated by sulphate of luteocobalt when alone, but when mixed with the sulphates of the cerite group more or less of a double sulphate of luteocobalt and yttria is always thrown down, and the same appears to be true for the sulphates of some other earths. In such cases the mixed sulphates of earths and luteocobalt should be gently heated in a muffle until the cobaltamine is completely decomposed and the excess of sulphuric acid is expelled. The residual sulphates of cobalt and the earths should then be dissolved in cold water, filtered, and again precipitated

* *American Chemical Journal*, xv., No. 7.

by sulphate of luteocobalt, allowing the mixture to stand twenty-four hours. The supernatant liquid appears then to contain all but the four cerite earths. This point is, however, not yet sufficiently proved, and I reserve it for further investigation.

The solution from which the double sulphates of the cerite earths and luteocobalt have been separated by decantation or filtration usually gives a more or less abundant crystalline precipitate on boiling. The filtrate from this again gives a precipitate with ammonia. The above stated facts are precisely those which we meet with in employing the alkaline sulphates in place of the sulphate of luteocobalt. I have also employed the sulphatochloride of luteocobalt, $Lc_2(SO_4)_2Cl_2$, as a precipitant, and find that double salts are sometimes formed which are much more insoluble than those obtained with the sulphate, excepting only in the cases of the four cerite earths. These contain chlorine as well as sulphuric oxide, and they are sometimes at least formed when sulphate of luteocobalt is added to a solution containing the chlorides of metals of the cerium and yttrium groups. Sulphate of roseocobalt gives in general the same result as sulphate of luteocobalt, only the salts formed in this case are more soluble in both cold and hot water. Experiments with the sulphates of xanthocobalt and croceocobalt have not yet led to valuable results. Certain sulphates of the earths appear to give with sulphate of luteocobalt only hydroxides of the metals, $R(OH)_3$. In this case it seems more probable that a true double sulphate is at first formed and then decomposed, sulphuric acid being set free.

The following results may be of interest in this connection. A portion of earths from Fergusonite sent me by Dr. Shapleigh was converted into sulphates; the cerite earths had been separated by sodic sulphate, and the solution of the earths gave no further precipitate with this. A solution of sulphate of luteocobalt gave no precipitate with this solution in the cold, but on boiling a very abundant crystalline precipitate, insoluble or very slightly soluble in boiling water. The filtrate from these crystals gave only a small precipitate with ammonia, so that the luteocobalt salt must have contained almost all the earths other than the cerite earths. These are known to consist chiefly of yttria. The crystalline precipitate obtained as above by boiling, and insoluble in boiling water, dissolved completely in a large quantity of cold water. The nitrates of roseocobalt and luteocobalt give, in many cases at least, finely crystalline precipitates with the nitrates of the earths. In certain cases, white gelatinous precipitates of hydroxides are formed at the same time, probably as in the case of the sulphates above cited, in consequence of the formation of double nitrates and their subsequent decomposition into free acid and hydroxide. This makes a new mode of differentiation which may prove to be of use, and to which I shall return hereafter. As an instance I may cite the case of the neutral nitrates of the gadolinite earths, from which the cerite earths have been separated by sodic sulphate. A strong solution of these nitrates gives with nitrate of roseocobalt, $Rc(NO_3)_3$, in a short time a bright orange, highly crystalline, and a dirty white, gelatinous precipitate. Both contain earths. The same is true for neutral nitrates from Samarskite, and from the cerite and monazite residues already mentioned. The nitrate of roseocobalt must be in excess. I have already stated that the action of the sulphates of roseocobalt and luteocobalt upon the sulphates of the earths closely resembles that of the alkaline sulphates, The advantage of using the cobaltamines consists, in part, in the fact that the double sulphates of these and the earths are highly crystalline and exceptionally well defined, and that they are in some cases at least very much less soluble than the alkaline double sulphates. The chief disadvantage is that the cobaltamines must be specially prepared for use, and that the most valuable of them—the sulphate of luteocobalt—is not easy to prepare in quantity and in a state of purity. Professor Morris Loeb has, however, found that sulphate of roseocobalt may be converted into sulphate of luteocobalt by heating with strong ammonia water under pressure, as for instance in sealed tubes; and, as the sulphate of roseocobalt is easily prepared, this process is perhaps the best.

A solution of sulphate of luteocobalt gives a very insoluble yellow crystalline precipitate with sulphate of thoria, $Th(SO_4)_2$. It gives also slightly soluble precipitates with uranic sulphate, UO_2SO_4, and with a solution of ferric alum which has undergone dissociation by solution. This last precipitate appears to have the formula $Fe_2O.(SO_4)_2+Lc_2(SO_4)_3$.

It is my hope to be able to return to the subject in greater detail.

Relations of the Oxides to Lactic Acid.—A portion of the oxides obtained from Samarskite by Dr. Shapleigh after the cerite oxides had been separated by sodic sulphate was boiled with pure lactic acid, and gave an amethyst-red solution. On standing, this solution gave two kinds of crystals, which were very distinct and well defined. These were beautiful red flat prisms, and distinct bright yellow granular crystals. The quantity was too small to permit a more thorough examination, and I did not obtain the same result a second time with other Samarskite oxides. In one experiment, however, the solution of the oxides was deep orange, and after a time deposited crystals with a fine orange colour.

The lactates of the cerite earths and of the Samarskite earths which have not been treated with potassic or sodic sulphate give beautiful white feathery crystals, which dissolve with difficulty in hot water.

Relations of Mercurous Nitrate and Mercuric Oxide to Cerite Earths.—A solution of mercurous nitrate gives in general no precipitate with neutral nitrates of the cerite earths. In one experiment, however, in which I employed nitrates from a commercial oxalate, added a solution of mercurous oxide, and then boiled with free mercuric oxide, the colour of the oxide changed to a greyish tint. After filtering and washing, the filtrate was found to contain abundance of didymium (Nd and Ps). The precipitate after washing with boiling water was heated to redness in a platinum crucible, when a clear yellow powder remained. This dissolved in dilute nitric acid to a colourless liquid, which gave no didymium bands with the spectroscope. On adding water to the nitric acid solution a beautiful bright yellow crystalline powder was thrown down. When the oxides were treated with sulphuric acid a white crystalline mass was formed. Hot water gave with this a fine bright yellow crystalline precipitate. I did not obtain these results with any other samples of cerite oxalates. So far as I am aware no known earths exhibit the reactions with nitric and sulphuric acids above described.

Relations of the Samarskite Oxides to Acid Molybdates, and to Phospho-tungstates und Phospho-molybdates.—To determine whether any of the oxides contained in Samarskite were capable of forming complex inorganic acids the following experiments were made with a bright yellow mixture of oxides prepared by Lawrence Smith's process with fluohydric acid. The quantity at my disposal was less than five grms., and I am not certain that the cerite oxides had been removed by sodic sulphate.

1. With 10 : 5 phospho-molybdate of ammonium. The mixed oxides dissolved very easily on boiling with solutions of the phospho-molybdate, giving a fine orange solution. The action of the solution of phospho-molybdate upon the oxides seemed to give instantly a crystalline mass, which on boiling with some excess of phospho-molybdate dissolved. The solution gave beautiful orange-brown crystals, but after twenty-four hours the solution was clear and had a fine rose-colour. This solution gave no absorption bands with the spectroscope. With ammonic oxalate it gave a white crystalline precipitate with a clear rose-red solution. This, on evapora-

tion to dryness in a platinum vessel, gave a rose-red mass, which, when heated, fused to a greenish mass. The white oxalate settled slowly. The orange crystalline salt dissolved almost completely in boiling water, but some yellow crystalline matter remained. On standing, the solution deposited crystals of a yellow salt.

2. With 14 : 6 molybdate of ammonium. A solution of 14 : 6 molybdate of ammonium (commonly written $7MoO_3.3(NH_4)_2O$) also readily dissolved the mixed oxides and gave a deep orange solution. On standing twenty-four hours this gave bright yellow and afterwards very beautiful glittering orange-red crystals. The two kinds of crystals re-dissolved gave with mercurous nitrate a pale yellow flocky precipitate, which, on boiling and standing, became bright yellow and highly crystalline. The least soluble crystals were also re-dissolved separately, and, after twenty-four hours, crystallised in beautiful prehnitic groups. The orange mother-liquor from these crystals gave the reaction with mercurous nitrate mentioned above. It seems probable from the above that 14 : 6 molybdate of ammonium gives at least two distinct salts.

3. With 24 : 2 sodic phospho-tungstate. A solution of this salt also dissolved the Samarskite oxides very readily on boiling, giving a fine orange-red solution which soon deposited an abundance of yellow needles. These dissolved readily in hot water to a yellow solution with an orange tint. Yellow needles quickly formed in abundance. After an hour the still slightly warm mother-liquor was poured off and allowed to stand. Two kinds of crystals separated,—very distinct, rather large granular orange crystals in much the larger quantity, and very small granular yellow crystals, differing much from the last in appearance. The two kinds of crystals were dissolved together in hot water, and after a time gave flocky masses of yellow crystals.

I did not succeed in obtaining the same results with other preparations of Samarskite oxides. This will not surprise those who have worked with the rare earths, and who have noticed the difference in the reactions which depends upon difference in the proportions of the mixed oxides. It has, I believe, escaped notice that the same occurs with mixtures of the different metals of the platinum group, as long since shown by Claus.

The compounds with molybdic oxide and with phospho-molybdic and phospho-tungstic acids may prove to be only salts of the earths, and not of complex acids. They appear to deserve further attention as means of separation. As the minerals belonging to the same group with gadolinite resemble each other very closely in their physical characters, it is possible that the yellow oxides above mentioned were not prepared from Samarskite, but from some other mineral.

Analyses 1 to 46 and from 69 to 122 inclusive were made by Mr. Edward L. Smith; from 47 to 68 inclusive by Mr. Wm. J. Karslake. My grateful acknowledgments are due to both.

ON THE

MINIMUM ELECTROMOTIVE FORCE NECESSARY FOR THE ELECTROLYSIS OF ALKALINE SALTS IN SOLUTION.

By C. NOURISSON.

As M. Berthelot has demonstrated (*Annales de Chim. et de Phys.*) there is in the work of electrolysis no occasion for separating the primary reactions from those known as secondary, but it is merely necessary to take into account the initial and the final state of the solution. I have sought, whilst observing this rule, to calculate from thermo-chemical data the minimum electromotive force necessary for the electrolysis of dissolved alkaline salts and then to verify experimentally the calculated result.

We take, *e.g.*, sodium chloride, admitting that there is total decomposition and then total combination of the elements. We distinguish four reactions which conjointly form the electrolysis :—

	Cal.
1. $NaCl = Na + Cl$, with absorption of	96·4
2. $H_2O = H_2 + O$ „ „	68·4
	164·8
3. $Na + O + H + Aq = NaOH$ dissolved with liberation of	111·8
4. Formation of oxides of Cl	6·0
	117·8

The difference is 164·8 − 117·8, or 47 cal., and it is therefore requisite that the electric current furnish work corresponding to 47 cal. in order to electrolyse 1 equiv. sodium chloride, always on condition that it effects no other work beside the electrolysis. The electromotive force then would be—

$$\frac{47}{23{\cdot}2} = 2{\cdot}02 \text{ volts},$$

a tension which we know is sufficient to electrolyse sodium chloride.

On calculating in the same manner we find for—

NaBr .. .. .. 40·6 cal. and 1·75 volt.
NaI . .. . 26·9 „ „ 1·16 „

Results verified by experience.

If we examine an oxy salt, *e.g.*, sodium sulphate—

	Cal.
1. $SO_4Na_2 = S + O_4 + Na_2$, with absorption of ..	329
2. $2H_2O = 2H_2 + O_2$ „ „ ..	136·8
	465·8
3. $S + O_3 + Aq$ = dilute SO_4H_2 with liberation of	142·5
4. $Na_2 + O_2 + H_2 + Aq = 2NaOH$ dissolved with liberation of	223·6
	366·1

Difference, 99·7 cal.

We remark that according to these equations there remains H_2 at the cathode and O at the anode, since the result is identical if we admit that the current simply decomposes the water and separates the sulphate into a free base and a free acid. We have then :—

Decomposition of H_2O	68·4 cal.	
Neutralisation of sulphuric acid	31·4 „	
	99·8 „	to be supplied by the current.

As sulphuric acid is bibasic, this figure must be divided by 2 to find the amount corresponding to 1 equiv., or—

$$\frac{99{\cdot}8}{2 \times 23{\cdot}2} = 2{\cdot}15 \text{ volts}$$

as the smallest electromotive force capable of decomposing sodium sulphate.

Sodium nitrate and chlorate give, in like manner, 48 cal. and 2·07 volts.

On examining the salts of other metals, those, *e.g.*, of potassium, we see that the results are alike, as it follows from the known fact that the difference between the formation-heats of potassium chloride and of potassa is the same as that between the formation-heat of similar compounds of sodium. It is thus for all the other salts of the alkaline metals. The work to be supplied is constant for the electrolysis of all the salts of one and the same acid.

But, according to Faraday's law, there is required an equal quantity of electricity to liberate an equivalent of the various simple substances. It results that if the work of electrolysis is constant for all the dissolved alkaline salts of one and the same acid the electromotive force will be constant also, since the work is proportional to the product of the quantity by the difference of potential.

But for the oxy-salts the work always consists in decomposing water and liberating an acid and a base, and as the neutralisation-heat of the acids is almost invariable, it results that the work of electrolysis will be the same for all the oxy-salts, and we may hence say that:—

The minimum electromotive force necessary for the electrolysis of a dissolved alkaline salt is constant on the one hand for all the oxy-salts, and on the other for all the haloid salts derived from the same acid.

Here follow the experimental results in support of this view:—

	Chlorides.	Bromides.	Iodides.	Sulphates.	Nitrates.	Chlorates.
K	1·97	1·74	1·15	2·40	2·32	2·45
Na	2·10	1·71	1·19	2·40	2·36	2·42
Li	2·01	—	—	2·43	2·45	—
Ca	1·95	1·71	1·16	—	2·28	—
Ba	1·94	1·72	1·17	—	2·37	2·48
NH_3	1·83	1·46	—	2·29	—	—
Calculated values..	2·02	1·75	1·16	2·15	2·07	2·07

These numbers which represent volts are not absolute, the graduation of the apparatus not being perfect, but they are mutually comparable and they have been obtained as follows:—

Let D be the difference of potential between the two extremities of an accumulator of a great yield but low tension (*e.g.*, 5 to 6 volts and 50 ampères). I measure this value directly by means of a voltmeter graduated in 50ths of volts. I then insert in the circuit the electrolytic bath containing the solution in question, and I read off again. Let *d* be the figure obtained, and E the electromotive force, we have—

$$D - d = E.$$

It is easy by means of a commutator to effect rapidly the numerous readings of D and *d*, of which we can take the mean. On the other part, knowing the resistance of the instrument, we calculate the intensity of the current. It was in my experiments at most $\frac{1}{1000}$ of an ampère and the resistance of the solution was practically nul, the electrodes being at least 30 square c.m. They were of platinum, distant from each other by 10 to 12 m.m., and separated by a porous septum.

The solutions compared contained each the same number of mols. per litre, and the fact of decomposition was each time verified at both poles. The escape of hydrogen was already visible.—*Comptes Rendus*, vol. cxviii., p. 189.

ON AN APPLICATION OF SODIUM SILICATE.

By G. GEISENHEIMER.

Whatever may be the purity of the chemical products employed in bleaching linen, there is no certainty of obtaining a perfect cleansing, even if the soda crystals are very white, the soap very rich in fatty matter, or the caustic soda without traces of sulphides or silicates. Frequently the linen either retains a rusty colour, or it is covered with large yellow spots, or it still retains all its pre-existing stains. To correct these defects, the bleacher increases the dose of causticity, prolongs the time of ebullition, and if he sometimes arrives at his object it is at the expense of the cloth which is scorched. It is observed that linen is worn out much less rapidly in the country where the lye is made from wood-ashes. Thus all the defects met with are generally imputed to the chemical products used, whilst they ought to be ascribed to the nature of the water employed. Some waters are reputed of good quality and others are rejected as unfit for bleaching. This distinction ought to disappear. In common waters only the salts of lime and magnesia have any influence, the salts of the other bases are in too small proportion.

Calcium bicarbonate is split up on ebullition or on the addition of soda, and forms a precipitate which adheres to the linen. It acts like a lake, and fixes on the fibre the yellowish colour of the alkaline solution where it takes its origin. These spots of lye resist both the subsequent washings and the oxidising agents. The calcium sulphate acts in the same manner; it is, further, brought back to the state of carbonate by the addition of soda-ash. It is also known that soaps are decomposed by the action of salts of calcium and magnesium.

If we use water which has been distilled or merely purified, the above-mentioned accidents no not occur. But in bleaching we cannot have recourse to the industrial methods of purification, which are too complicated; a simpler method is required. The calcareous water is rendered inoffensive by the addition of an alkaline silicate, the essential quality of which is complete solubility in water.

We obtain it easily by mixing with anhydrous sodium carbonate in powder from 10 to 20 per cent of a saturated solution of sodium silicate, $NaO2SiO_2$.

The carbonate tending to form the hydrate—

$$NaO,CO_2+10HO$$

absorbs the water of the solution and becomes, so to speak, the support of the silicate. In this form this salt is easily transported, and preserves its solubility, whilst no silicate obtained directly by fusion is entirely soluble.

In the lye the silicate forms with the salts of calcium and magnesium a flocculent precipitate which deposits quickly, is not at all adhesive, and on ebullition becomes pulverulent as sand. In solution in a purified water all the lixivial products are usefully employed; further, as neither caustic soda nor sodium carbonate is wasted, we may calculate the quantities strictly necessary, and avoid thus any hurtful and costly excess.

Experiment has shown that a very small quantity of caustic soda is needful, it is useful to "prime" the saponification of the fatty matters which the alkaline carbonate then continues in a manner less energetic and less dangerous for the tissues.

On analysing the active principles extracted from the wood-ashes we find solely sodium or potassium carbonate and silicate.—*Comptes Rendus.*

The Water Vibrios in the Etiologie of Cholera.—According to the studies of Sanarelli, the idea of the morphological unity of the cholera bacillus must be abandoned, since there exist different varieties of vibriones morphologically distinct, which are capable of producing in man and in the lower animals one and the same type of cholera, clinically identical. Koch's bacteriological diagnosis of cholera, as recently established, agrees neither with the idea of a limited monomorphism, nor with the assumption of a polymorphism of the vibriones, since in every impure water we may find pathogenous microbia which possess quite the same characters as the specific exotic vibriones. In addition to the morbific forms originating in the water, which exactly resemble those from the bowel, there are found in water a number of non-pathogenous microbia which approach the former very closely, so that they may be regarded as varieties capable, under certain circumstances, of resuming their former (?) malignant properties. This constant occurrence of pathogenic microbia in all sewage is a proof of the great importance of the pollution of water for the origin and the spread of cholera. The water-vibrios and those of cholera dejections are in every respect very closely allied, which points to a common origin. Virulent water vibriones do not long retain their malignant character; they gradually disappear along with the other characteristic properties of the vibriones, such as the formation of nitrites and of indol.—*Annales de l'Inst. Pasteur* and *Chemiker Zeitung.*

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 18th, 1894.

Dr. Armstrong, President, in the Chair.

(Concluded from p. 59).

*100. "*Contributions to our Knowledge of the Aconite Alkaloids.* IX. *The Action of Heat on Aconitine.*" By Wyndham R. Dunstan, M.A., F.R.S., and F. H. Carr.

The authors find that when aconitine is heated at its melting-point (188—190°) it loses about 10 per cent of acetic acid, which distils over, leaving a new alkaloid which they propose to name *pyroconitine*,—

$$C_{33}H_{45}NO_{12} = C_2H_4O_2 + C_{31}H_{41}NO_{10}.$$

Pyraconitine is obtained in the form of an amorphous varnish, sparingly soluble in water, but readily in alcohol, chloroform, and ether. It has no effect on polarised light, and is not poisonous in small doses. The alkaloid readily dissolves in acids, forming salt which can be crystallised.

Pyraconitine hydrobromide, $C_{31}H_{41}NO_{10}\cdot HBr$, forms prismatic crystals melting at 280° (corr.). The salt is readily soluble in water and alcohol, but is not dissolved by ether. It is best crystallised from a mixture of alcohol and ether. In aqueous solution it is lævorotatory: $[\alpha]_D = -46{\cdot}47°$.

Pyraconitine hydrochloride, $C_{31}H_{41}NO_{10}\cdot HCl$, crystallises in rosettes from a mixture of alcohol and ether. It melts at 249°.

Pyraconitine hydriodide, $C_{31}H_{41}NO_{10}\cdot HI$, also crystallises in rosettes, which become yellow when exposed to air. It melts at 220·5° (corr.).

The solutions of these salts have a bitter taste, but are not toxic, at all events in small doses.

Pyraconitine aurichloride, $C_{31}H_{41}NO_{10}\cdot HAuCl_4$, is thrown down as a pale yellow precipitate when auric chloride is added to a solution of the hydrochloride. No aurichlor-derivative could be obtained.

Pyraconitine and its salts readily undergo hydrolysis when heated with dilute acid or with water in a closed tube. Potash and soda quickly hydrolyse the alkaloid, even in the cold, but ammonia does so only very slowly. The sole products of hydrolysis are *benzoic acid* and an alkaloid which has been named *pyraconine*,—

$$C_{31}H_{41}NO_{10} + H_2O = C_7H_6O_2 + C_{24}H_{37}NO_9.$$

Pyraconine is an amorphous base resembling aconine in its properties, but differing from it in several respects. It is soluble in both water and ether. The aqueous solution has a somewhat sweet taste, and is lævorotatory $[\alpha]_D = -90{\cdot}99°$. It combines with acids to form crystalline salts which are very soluble in water.

Pyraconine hydrochloride, $C_{24}H_{37}NO_9HCl$, crystallises from water in cubes containing 1 mol. of water. It melts at 159° (corr.), and is soluble both in alcohol and in water. The aqueous solution is lævorotatory $[\alpha]_D = -102{\cdot}07°$.

Pyraconine aurichloride, $C_{24}H_{37}NO_9\cdot HAuCl_4$, is a pale yellow amorphous precipitate.

The salts of aconitine also furnish pyraconitine, losing acetic acid when heated at about 190°. Isaconitine and aconine, however, do not undergo a similar decomposition. The authors consider it probable that the production of acetic acid from aconitine may serve as the basis of a process for the estimation of this alkaloid.

*101. "*Contributions to our Knowledge of the Aconite Alkaloids.* X. *Further Observations on the Conversion of Aconitine into Isaconitine.*" By Wyndham R. Dunstan, M.A., F.R.S., and F. H. Carr.

In a former communication the authors showed that when certain aconitine salts are heated at 100° in slightly acid solution they are very slowly changed into the salts of isaconitine. They have since found that this conversion may be effected with great rapidity by heating a neutral aqueous solution in a closed tube at 120—130° during from two to three hours, when the aconitine salt disappears, often so completely that the solution produces a tingling sensation on the tongue. The isaconitine is separated from the solution which has been rendered alkaline with ammonia by repeated extraction with ether.

It has also been proved that the production of isaconitine invariably precedes the hydrolysis of aconitine into aconine and benzoic acid, not only when the hydrolysis is effected by acid, as was pointed out in a previous paper, but also, as has now been found, when water alone is used as the hydrolytic agent. In previous experiments the formation of isaconitine during the hydrolysis of aconitine in presence of alkali could not be proved, owing to the rapidity with which aconine is produced. If, however, a considerable excess of an aqueous solution of soda be added to a solution of an aconitine salt, and the precipitated alkaloid be allowed to stand in contact with the cold alkaline solution until some of the alkaloid is dissolved, extraction with ether separates a notable quantity of isaconitine, as well as the unchanged aconitine. It therefore appears that the non-toxic aconine is really the product of the hydrolysis of the non-toxic isaconitine into which the aconitine first changes.

The observations recorded in the foregoing paper, which prove that aconitine salts as well as the alkaloid lose acetic acid when they are heated, led the authors to look for the production of this acid when solutions of these salts are heated. It has been found that some acetic acid is formed when aconitine salts are heated with water in the manner above described, and also when these salts or the alkaloid are hydrolysed. They are at present engaged in investigating the origin and amount of the acetic acid produced under various conditions, and also in determining whether pyraconitine is formed in corresponding quantity or whether aconitine may not be an acetyl derivative which loses its acetyl group on hydrolysis. If the latter view should prove to be correct, the nomenclature and formula of aconitine derivatives will need entire revision.

102. "*Interaction of Benzylamine and Ethylic Chloracetate.*" By A. T. Mason, Ph.D., and Goodlatte R. Winder, Ph.D.

The action of benzylamine on ethylic chloracetate is similar to that of ammonia and methylamine, the first product being the ethylic salt of benzylamidoacetic acid, $Ph\cdot CH_2\cdot NH\cdot CH_2\cdot CO_2Et$, which, however, undergoes condensation, even at the ordinary temperature, two molecules of the ethylic salt uniting, and two molecules of alcohol being formed together with dibenzyl α-γ-diacipiperazine,—

$$C_6H_5\cdot CH_2\cdot N\begin{matrix}CO\cdot CH_2\\ CH_2\cdot CO\end{matrix}N\cdot CH_2\cdot C_6H_5.$$

103. "*Condensation Products from Benzylamine and Several Benzenoid Aldehyds.*" By A. T. Mason, Ph.D., and Goodlatte R. Winder, Ph.D.

The products obtained are similar in their properties and mode of formation to those obtained from the primary paraffinoid and benzenoid amines and the benzenoid aldehyds. The following are described:—

Benzylidenebenzylamine, $C_6H_5\cdot CH_2\cdot N{:}CH\cdot C_6H_5$.

o-Hydroxybenzylidenebenzylamine,—

$$C_6H_5\cdot CH_2\cdot N{:}CH\cdot C_6H_4\cdot OH.$$

p-Hydroxybenzylidenebenzylamine,—

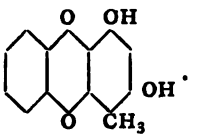
$$C_6H_5\cdot CH_2\cdot N{:}CH\cdot C_6H_4\cdot OH.$$

104. "*Constitution of Rubiadin.*" By Edward Schunck, Ph.D., F.R.S., and Leon Marchlewski, Ph.D.

The authors arrive at the conclusion that rubiadin does not contain a methoxy-group, but has a methyl group attached to the nucleus, as it does not yield methyl iodide on distillation with iodhydric acid, and also remains unchanged when heated with concentrated sulphuric acid at

180°. It was found, moreover, that when oxidised with chromic acid it gives phthalic acid, from which it may be inferred that the methyl and hydroxyl groups are attached to the same nucleus. These and other facts, such as those described in their first communication, render it certain that rubiadin cannot be identical with any possible methylalizarin or methylquinazarin, and that it must be regarded as a methylpurpuroxanthin.

Two alternative formulæ are therefore proposed. By condensing benzoic acid with metadihydroxyparatoluic acid a substance was obtained which had many properties in common with rubiadin, but differed as regards melting-point and the melting-points of the respective acetyl derivatives. This decided the authors in favour of the second formula given by them, viz.,—



105. "*The Monalkyl Ethers of Alizarin.*" By EDWARD SCHUNCK, Ph.D., F.R.S., and LEON MARCHLEWSKI, Ph.D.

Monomethylalizarin melts at 228—229°, and yields an acetyl derivative melting at 186—187°. Monethylalizarin melts at 188—189°; its acetyl derivative at 141°. It is pointed out that in these compounds the alkyl has probably displaced the hydrogen atom in the β-OH group in alizarin. Experiments were made with a view to obtain ethers of alizarin isomeric with these, but without success.

106. "*Ruberythric Acid.*" By EDWARD SCHUNCK, Ph.D., F.R.S., and LEON MARCHLEWSKI, Ph.D.

This glucoside, like all glucosides hitherto known, is not acted on by phenylhydrazin, and therefore does not contain an aldehyd group. Its constitution must, therefore, be represented in accordance with the formula of Tollens for glucose. When subjected to the action of benzoyl chloride in presence of sodic hydrate, ruberythric acid yields, according to the concentration of the soda solution, either a hepta- or a hexa-benzoyl derivative.

107. "*The Colouring Matter of the Indian Dye-stuff 'Tesu.'*" By J. J. HUMMEL and W. CAVALLO, Ph.D.

This yellow dye-stuff consists of the dried flowers of *Butea frondosa*. The dyeing power of the flowers as sold is comparatively slight, but is increased by boiling with diluted acid, the glucoside of the dye-stuff becoming hydrolysed.

By boiling the aqueous extract with sulphuric acid, then extracting with ether, and purifying the product by crystallising it from alcohol and water, the authors have obtained about 1 per cent of a substance crystallising in almost colourless needles, melting, when rapidly heated, at 217°. On analysing this, numbers were obtained (C = 65·5 and 65·65, H = 4·93 and 4·67) corresponding with the formula $C_{15}H_{14}O_5$. A large quantity of material is now being operated on.

PHYSICAL SOCIETY.

Ordinary Meeting, January 26th, 1894.

Prof. A. W. RÜCKER, M.A., F.R.S., President, in the Chair.

MR. J. W. KEARTON read a "*Note on a New Mode of making Magic Mirrors.*"

The author's first idea was that the magic properties were due to differences in reflecting power, but experiments showed this to be improbable, and indicated that the patterns visible by reflected light were due to slight concavities in the surfaces. Several methods of producing such changes of curvature were tried, such as electro-depositing and electro-etching; the plate being subsequently polished to remove sharp edges.

The method found most satisfactory was to draw the figures on polished brass coated with wax, and etch them by immersing in nitric acid, subsequently scouring with charcoal, Sheffield lime, and swans-down calico until all direct traces of the figures disappeared. The scouring rounds off the edges and makes the depressions concave, the two eventually forming one concave sweep, which makes itself visible when light is reflected from it on a screen. To obtain satisfactory results with figures having broad and narrow lines it was found necessary to paint over with hot wax the fine lines and the outer edges of the broad ones after the first immersion; a second immersion etched the middle parts of the broad lines deeper. By repeating the process the broad lines were etched roughly concave in steps, and the scouring made these curvatures continuous. Figures in relief, showing the patterns in shade on reflection, were obtained by painting the pattern on the plate in sealing-wax dissolved in naphtha and etching away the uncovered portions by an immersion of one or two seconds. A number of mirrors with patterns in intaglio and relief were exhibited to the meeting.

Prof. S. P. THOMPSON said the chief interest of Mr. Kearton's work was that he had succeeded in producing mirrors by a process which Prof. Ayrton had found unsuccessful. The spherical polisher used by Mr. Kearton might have something to do with the result obtained. Some of the mirrors had been gilt after polishing and the reflected pattern improved thereby.

Prof. AYRTON said he was greatly interested to see that mirrors could be produced by the chemical method. The polisher used by the Japanese was the flat end of a tight bundle of special straw cut crosswise. When the true explanation of the magic properties was found out, the chemical method was not pursued further.

The Rev. F. J. SMITH mentioned that he had produced magic properties on silvered glass by the inductoscript method. Although no markings could be seen directly, the pattern showed itself when light was reflected from the surface to a screen.

MR. W. B. CROFT, M.A., read a paper on "*Some Observations in Diffraction,*" and exhibited a large number of photographs of diffraction figures obtained under different conditions.

The first series exhibited related to diffraction from parallel light (diffraction of Fraunhofer and Schwerd) and were obtained by placing various combinations of thin circular lines of light on a dark glass plate before the object glass of a telescope focussed on a star. Spectral images of the star are formed by interference from the edges of the lines, thus giving diffraction patterns whose form depends on the shape of the aperture employed.

The next series illustrated diffraction in shadow (Fresnel's diffraction), and were produced by condensing light on a minute pinhole, and placing the object between the hole and a microscope eye-piece. Beyond the eye-piece, the camera used for photographing the phenomena was placed. Permanent records of remarkably good diffraction figures were obtained in this way, both of the combination of circles above mentioned and of various other objects and geometrical forms.

After showing geometrically that diffraction bands from narrow obstacles and openings were wider than those from broader ones, the author explained the conditions necessary for making the bands visible, and pointed out the distinction between internal and external bands. Prominent amongst the photographs were several showing "Arago's white spot" at the middle of a shadow; and in particular this well-known phenomenon was shown as produced by so large an object as a threepenny-piece.

Speaking of diffraction in a microscope, the author said little doubt need exist as to whether an image represented the real object or a diffraction modification thereof, for

the latter were usually of a more misty and complicated character.

Departing somewhat from the subject of diffraction, an excellent photograph of conically refracted pencils was shown, consisting of circular lines of light produced by passing light from pinholes through a crystal of arragonite.

Dr. Johnstone Stoney thought the obtaining of permanent records of diffraction phenomena of great importance, and was particularly interested in the photograph showing conical refraction.

Prof. S. P. Thompson said he had never seen diffraction effects exhibited to an audience so well before. He noticed that in several of the photographs Arago's spot was unintentionally shown to perfection, in the shadows of dust particles.

The President greatly appreciated the fact that the conical refraction photograph had been exhibited for the first time before the Physical Society.

A "*Note on a New Photometric Method, and a Photometer for same*," was read by Mr. J. B. Spurge.

The method consists in using two diffusing screens (illuminated respectively by the lights to be compared) as secondary sources, and adjusting to equality the luminosity of equidistant internal surfaces by varying the apertures through which the light passes from the screens to these surfaces. By reducing the sizes of the apertures, the author has been enabled to compare lights of different colour; for when of sufficiently feeble intensity, coloured lights are indistinguishable from white or grey.

The photometer is made up of two tubes mounted at 45° to an axis, about which one of them is capable of rotating. When in the same horizontal plane, the axes of the tubes form the sides of an isosceles right-angled triangle, at the middle of whose hypothenuse the light to be tested is placed; this illuminates one of the screens, whilst the standard light shines on the other. These screens, used as secondary sources, are situated a short distance away from the outer ends of the tubes, whilst the inner surfaces of the near ends of the tubes are viewed by means of a mirror. By turning the movable tube about the inclined axis, and rotating the source about a vertical axis, the illuminating effect of the source in any direction can be tested.

Capt. Abney said the law of inverse squares was not true for weak lights, for the proportions in which the light from sources of equal intensity had to be reduced to appear white or grey depended greatly on the colour, being much greater for violet than for red. Only for the yellow-green rays was the ordinary law of illumination true when the intensities were feeble.

Mr. Blakesley, Prof. S. P. Thompson, and the President also took part in the discussion.

OBITUARY.

THE LATE EDMOND FRÉMY.

On Saturday, February 3rd, French chemical science lost one of its most distinguished representatives in the person of Prof. Edmond Frémy. The late eminent *savant* was born at Versailles, and had reached his eightieth year. He received his first instruction in chemistry from his father. In 1831 he received an appointment at the Polytechnic School, where he afterwards obtained the chemical chair, which he filled honourably and successfully for many years. As a teacher of chemistry he took a high rank; his pupils, some of whom give promise of future eminence, have commenced a special chemical paper as their organ.

His first published researches appeared as far back as 1835. He excelled in the synthesis of minerals; thus he produced rubies and sapphires identical with the natural specimens, not merely in chemical composition, but in crystalline form, hardness, colour, and lustre. He was appointed technical director of the celebrated works at St. Gobain. He studied ozone in conjunction with Becquerel.

In his latter years he came forward as a persistent opponent of M. Pasteur, and, of course, of the zymotic theory of disease and of the microbian origin and character of the process of fermentation.

As late as 1881 he undertook to superintend the compiling and publication of an encyclopædia of chemistry, which will shortly appear, and which is eagerly expected.

The *Comptes Rendus* and other leading French scientific journals abound in valuable memoirs from his pen.

CORRESPONDENCE.

EXAMINATIONS.

To the Editor of the Chemical News.

Sir,—In a letter which appeared in the Chemical News, vol. lxix., p. 60, my friend Dr. Tilden complains that a student (? of his) has passed the Examination in Chemistry and Chemical Physics at the Conjoint Board although it appeared from the result of an examination at Mason College that "he knew nothing at all." From this he infers that either "private instructions have been issued to the Board (? of Examiners) that the examination in chemistry is to be a farce," or "the examiners in chemistry are systematically neglecting their obvious duty," and continues "I cannot perceive a way of escape from these alternatives."

Might I suggest that there is a third possible cause of this discrepancy, namely, the system of examination universally adopted in this country. I allude to the setting printed papers containing a limited number of questions, perhaps eight or ten only, assigning marks for the answers given, and passing the candidate if the total exceeds a certain fixed minimum. This applies, practically speaking, to all science examinations, the London University, the Victoria University, the Science and Art Department Examinations in Science, as well as to the Conjoint Board—possibly also to Mason College, as Dr. Tilden in his letter says of the aforesaid student "I gave him 5 per cent of marks *pro formâ*." As long as this system is in vogue, cases of the kind will abound, for at such examinations it is, to a very great extent, a matter of chance with the majority of candidates whether they pass or not. Out of eight or ten questions it may happen that a candidate, like the one who "knew nothing at all," is able to answer half a dozen fairly well, especially if he has been taught the art of passing examinations. He passes. Another candidate, who perhaps knows five times as much chemistry, can only answer four questions—of course he does not pass. This is the beauty of the system if we could only be brought to see it.

In conclusion, might I be allowed to say that when Dr. Tilden wrote, he did not, I think, realise that he was making a charge of dishonesty against the Examiners to the Conjoint Board, or in the other alternative that that Board—including as it does the most honourable and honoured members of the Medical Profession—*and the Examiners* had entered into a mean and dishonourable conspiracy to deceive the public. I am sure Dr. Tilden is the last person to knowingly make accusations of this kind.—I am, &c.,

Charles E. Groves.

Guy's Hospital, London,
February 5, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 4, January 22, 1894.

In the Session of January 22 the Perpetual Secretary announced the death of Sgr. Scacchi, Corresponding Member of the Section of Mineralogy. M. Pagneul was then elected a Corresponding Member of the Section of Rural Economy, *vice* the late Paul de Gasparin.

Minimum Electromotive Force necessary for the Electrolysis of Dissolved Alkaline Salts.—M. C. Nourisson.—(See p. 68).

An Application of Sodium Silicate.—G. Geisenheimer.—(See p. 69).

Certain Phosphochromates.—Maurice Blondol.—Hydrated phosphoric acid is capable of forming with chromic acid several double acids. In the present paper the author describes the well-defined and remarkably stable salts obtained by saturating with potassa certain mixtures of these two acids. These salts answer to the formulæ $PO_3.8CrO_3.3KO$ and $PO_3.4CrO_3.2KO.HO$. The presence of sulphuric acid or of molybdic acid in these mixtures gives rise to complex salts, which will form the subject of a future communication.

Action of Sulphuric Acid upon Wood Charcoal.—A. Verneuil.—This paper will be inserted in full.

Studies on the Chemical Properties of the Alcoholic Extract of Beer Yeast: Formation of Carbonic Acid and Absorption of Oxygen.—J. de Rey-Pailhade.—It has been known since Spallanzani that tissues recently detached from the living organism consume oxygen and produce carbonic acid, whether in the air or in an inert gas such as nitrogen. Gautier has generalised these facts when studying the products of the autonomous action of the muscular tissue separated from the living being and secluded from the action of microbia. I have shown some years ago that the tissues, if ground up with sulphur, evolve hydrogen sulphide. My latest experiments show that the proximate principles themselves produce these phenomena if extracted with suitable solvents, and that these effects appear independent of any figured ferment.

MEETINGS FOR THE WEEK.

MONDAY, 12th.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "The Detection and Measurement of Inflammable Gas and Vapour in the Air," by Frank Clowes, D.Sc.
TUESDAY, 13th.—Royal Institution, 3. "Locomotion and Fixation in Plants and Animals," by Prof. Charles Stewart, Pres.L.S.
—— Society of Arts, 8. "Modern Development of Illustrated Journalism," by Horace Townsend.
—— Medical and Chirurgical, 8.30.
—— Institute of Civil Engineers. 8.
—— Photographic, 8. (Anniversary).
WEDNESDAY, 14th.—Society of Arts, 8. "The St. Pancras Electric Light Installation," by Henry Robinson.
—— Pharmaceutical, 8.
THURSDAY, 15th.—Royal, 4.30.
—— Royal Institution, 3. "The Past and Future of Mountain Exploration," by W. Martin Conway, M.A., F.R.G.S.
—— Society of Arts, 4.30. "Experiences at the Court of Afghanistan," by John A. Gray.
—— Chemical, 8. Ballot for the Election of Fellows. "Determination of the Available Mineral Plant Food in Soils," by Bernard Dyer, D.Sc. "Aërial Oxidation of Turpentine and Essential Oils," by C. T. Kingzett.
FRIDAY, 16th.—Royal Institution, 9. "Bacon's Key to Nature," by Prof. Nichol, M.A., LL.D.
—— Geological, 3. (Anniversary).
—— Quekett Club, 8. (Anniversary).
SATURDAY, 17th.—Royal Institution, 3. "Light, with special reference to the Optical Discoveries of Newton," by the Right Hon. Lord Rayleigh, F.R.S.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

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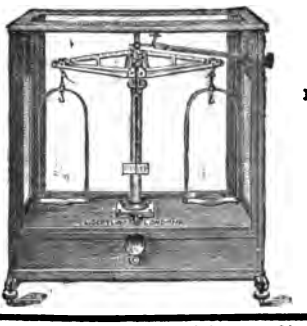

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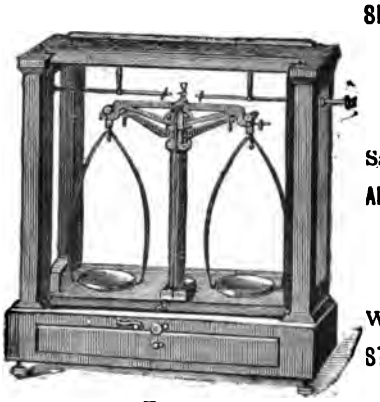

FIG. 3a.

SHORT BEAM BALANCE, No. 10a, Fig. 3a, to carry 100 grammes in each pan, and turn to 1-10th milligrm. Steel knife-edges, agate planes, two rider apparatus, and new improved arrangement for arrest of pans £8 15 0
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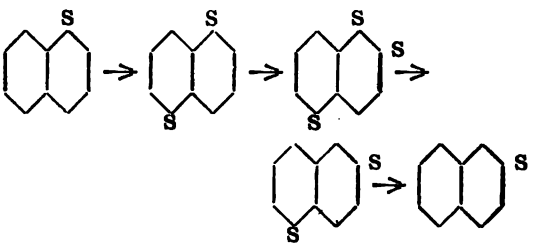
THE CHEMICAL NEWS.

Vol. LXIX., No. 1786.

THE INVESTIGATION OF ISOMERIC NAPHTHALENE DERIVATIVES.*

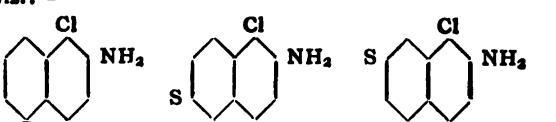
In previous reports attention has been over and over again directed to the *alpha-law of substitution* as the *dominant law* in the case of naphthalene, and to the numerous apparent departures from this law observed in the formation of sulphonic acids. Most interesting examples of the formation of α-derivatives are afforded by Cleve's recent invaluable observations on the behaviour of the chlorides of ten of the chloronaphthalenesulphonic acids on nitration ("Ofversigt af Kongl. Vetenskaps-Akademiens Förhandlingar," 1892, No. 9, presented Nov. 9; 1893, Nos. 2, 3, and 5, presented February 8, March 14, May 9). His results are displayed in a subsequent diagram, in which also the properties of the various derivatives are indicated, as the Swedish publication in which they are described is not generally available. The formula of the chlorosulphochloride is given in the first column of symbols; that of the resulting nitro-derivative or derivatives in the second; and that of the corresponding trichloronaphthalene obtained by the action of phosphorus pentachloride in the third. In the table of β-derivatives the results obtained by Dr. Wynne and the writer on sulphonating the β-chlorosulphonic acids† are included for comparison with those obtained on nitrating their chlorides. It will be seen that in the case of the α-chloro-acids the nitro-group in every instance takes up the "opposite" α-position; only in two cases are β-compounds obtained. In the case of the β-chloro-acids the nitro-group assumes the α-position *contiguous* to the β-chlorine atom—a most interesting and significant result.

The results obtained on nitration are strikingly different from those attending sulphonation; it can scarcely be doubted, however, that in the case of sulphonic acids the formation of β-acids is due to secondary changes, but opinions differ as to the nature of these. It appears to be commonly supposed that when sulphonation takes place at high temperatures and in presence of excess of acid, α-sulphonic groups become split off, and that sulphonation then occurs in β-positions; Dr. Wynne and the writer have been unable to discover any proof of direct sulphonation of the β-position, and incline to the belief that the formation of β-sulphonic derivatives is either the outcome of isomeric change or—and probably most frequently—of polysulphonation followed by hydrolysis. Thus, naphthalene-β-sulphonic acid is not‡ improbably the final product of the following series of changes:—



We have in a previous report directed attention to the fact that the polysulphonic acids which can be obtained by sulphonation are of certain types, and that there is, in fact, an invincible objection on the part of two SO_3H groups—under conditions thereby prevailing—to remain in either contiguous, or para-, or peri-positions. During the year we have been able to examine three of the naphthalenedisulphonic acids which cannot be obtained by direct sulphonation, *i.e.*, the 1 : 2, 1 : 4, and 1 : 1' acids, having prepared these, and the 2 : 3 : 2'-naphthalenetrisulphonic acid by an indirect method communicated to us by Dr. Duisberg (*cf. Chem. Soc. Proc.*, 1893, p. 166). With the aid of these acids and of others prepared by the same method we hope to further elucidate the phenomena of sulphonation.

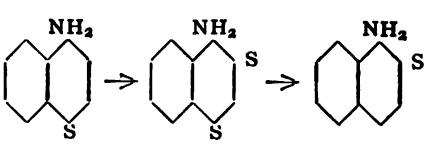
We have ascertained that of the three acids prepared by sulphonating chloro-β-naphthylamine hydrochloride, viz.:—



No. 1. No. 2. No. 3.

Nos. 2 and 3 are of independent origin; in other words, that, although both can be obtained from No. 1, No. 2 is not convertible into No. 3 under the conditions which admit of the conversion of No. 1 into Nos. 2 and 3. It is noteworthy that, in the formation of the No. 2 and No. 3 acids, chloronaphthylaminedisulphonic acids always accompany the two monosulphonic acids, and the investigation of these compounds, so far as it has progressed, affords further evidence in favour of our view of the complexity of the phenomena underlying the formation of β-sulphonic acids (*Ibid.*, 1890, p. 133).

Another case which may be referred to is that of the formation of 1 : 2-α-naphthylamine-β-sulphonic acid from naphthionic acid (1 : 4), which is effected by heating the sodium salt of the latter at about 200°. It appears probable to us that the change involves the formation of a disulphonic acid, which then undergoes hydrolysis, yielding the ortho-acid, thus:—

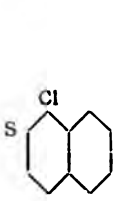
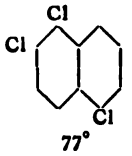
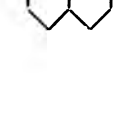
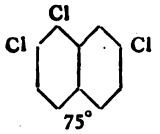
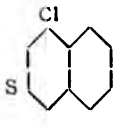
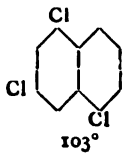
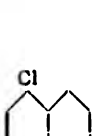
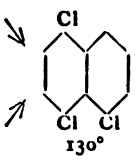
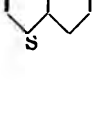
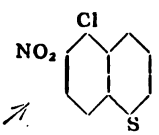
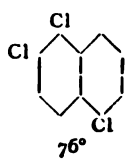
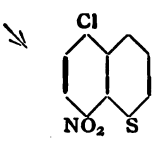
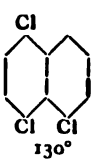
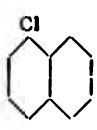
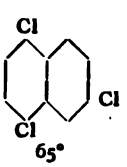


The production of disulphonic acid may be the outcome either of direct interaction of two molecules of the monosulphonic acid or of the action of acid sulphate formed by the agency of traces of water unavoidably present in the salt. It has actually been observed that hydrated potassium 1 : 2 : 4-α-naphtholdisulphonate yields the ortho-mono sulphonate when heated (*cf.* Conrad and Fischer, *Liebig's Annalen*). The superior stability of the ortho- as compared with the para-sulphonate thus brought into

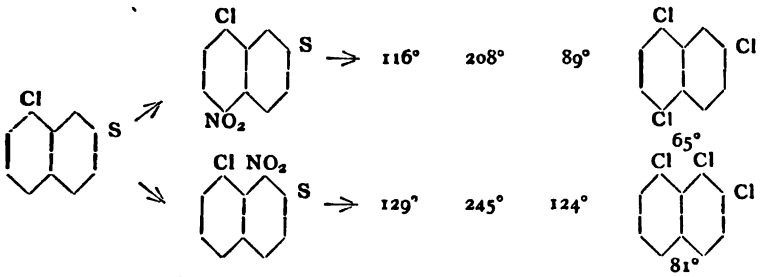
* Seventh Report of the Committee, consisting of Professor W. A. Tilden and Professor H. E. Armstrong (Secretary). Drawn up by Professor Armstrong.—Read before the British Association (Section B), Nottingham Meeting, 1893.

† The results of our examination of the sulphonation products of all the obtainable chloronaphthalenesulphonic acids are yet to be published. It may not be out of place to state that the work which was expressly reserved in 1890—the examination of the sulphonation products of the chloronaphthalenemonosulphonic acids (first notice, *Proc. Chem. Soc.*, 1890, p. 131), and of the corresponding naphthylaminemonosulphonic acids (first notice, *Proc. Chem. Soc.*, 1890, p. 128)—is nearly completed. As the object of the work is the determination of the positions assumed by the entering sulphonic radicle in the two classes of derivatives, there is little to be gained in publishing the results until the constitution of each disulphonic acid has been ascertained beyond question. This has involved characterising the trichloronaphthalenes more definitely than by melting-point determinations, and, as in the case of the dichloronaphthalenes (*Proc. Chem. Soc.*, 1890, p. 77; *Brit. Assoc. Rep.*, 1891), this is being carried out mainly by examining the acids obtained by sulphonating each of the fourteen isomeric trichloronaphthalenes (first notice, *Proc. Chem. Soc.*, 1890, p. 76).

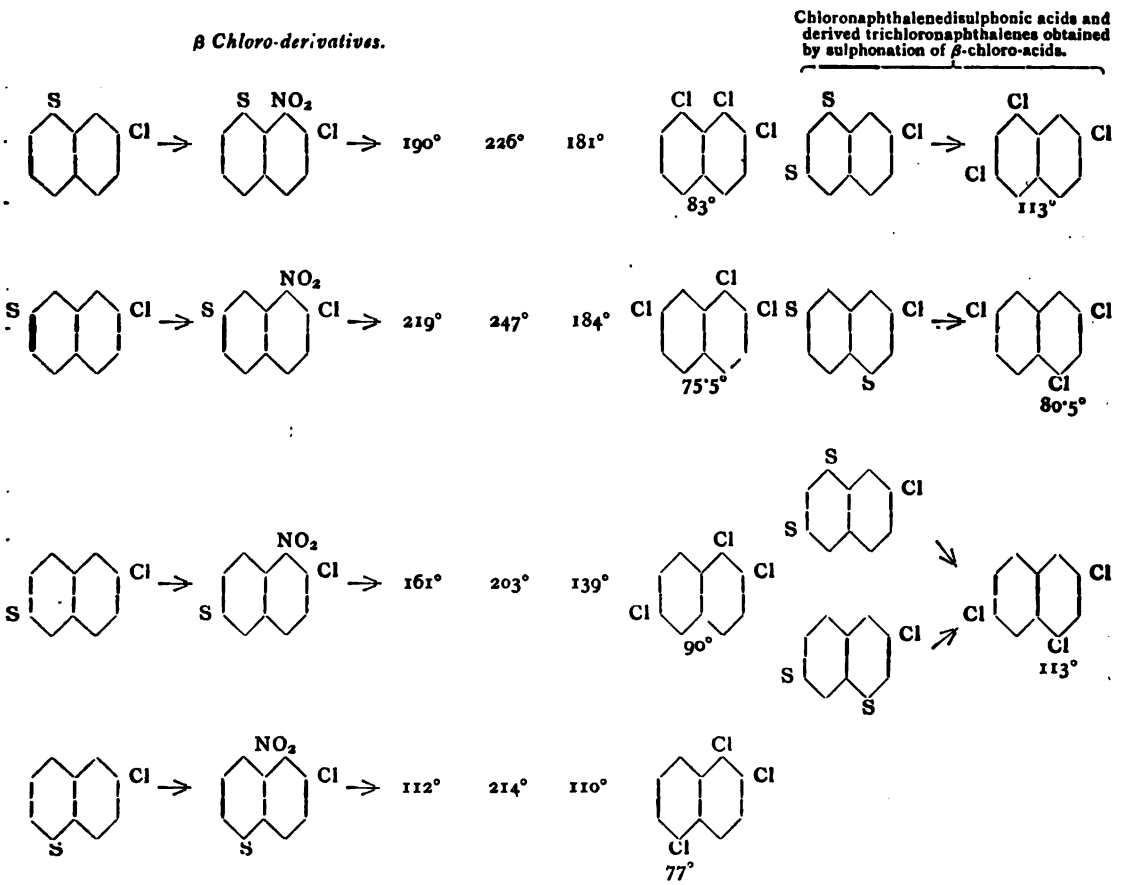
α-Chloro-derivatives.

	Melting-point of Chloro-nitro-sulphonic			
	Chloride.	Amide.	Ethylic salt.	
	151°	220°	116°	 77°
	182°	231°	—	 75°
	130°	188°	—	 103°
	127°	181°	—	 130°
	150°	233°	—	
	118°	220°	—	 76°
	134°	—	—	 130°
	161°	188°	123°	 65°

α-Chloro-derivatives (continued).



β Chloro-derivatives.



evidence in the case of both naphthol and naphthylamine is highly remarkable, bearing in mind the extreme instability of the corresponding benzene derivatives, and is evidence that the mere contiguity of an amido- or hydroxyl-group does not condition instability. The special properties of the β-sulphonic derivatives of naphthalene are doubtless a consequence of a structural peculiarily of the cycloid. It is especially from this last point of view that observations such as are here alluded to are of particular interest, and it may be permitted to draw attention to them as illustrating the circumstance that facts which in themselves are of no special value may become of more than usual interest when considered in connection with the larger problems underlying all investigations of details.

In the course of the further study of the action of bromine on beta-naphthol derivatives, interesting results have been obtained which may be here mentioned. If an aqueous solution of potassium 2 : 2'-beta-naphtholsulphonate be subjected to the action of even a large excess of bromine, potassium bromohydroxynaphthaquinonesulphonate is produced, together with a very small proportion of dibromohydroxynaphthaquinone; but if an aqueous solution of this quinonesulphonate be warmed with bromine it becomes oxidised to a brominated sulphophthalic acid; apparently, in the former case, the pre-

sence of hydrogen bromide in excess prevents the bromine acting as an oxidising agent. It is easy to obtain a monobromosulphonate and the quinonesulphonate by the action of bromine on an aqueous solution of Schaeffer's salt, but the preparation of the intermediate di- and tri-bromosulphonates is very difficult. If, however, the *salt* be suspended in muriatic acid it is easy to convert it wholly into tribromosulphonate and to avoid the production of quinonesulphonate. Recently it has been ascertained that if 2 : 3′ betanaphtholsulphonic acid be dissolved in muriatic acid it is wholly converted into tetra-bromo-beta-naphthol by the mere addition of an excess of bromine; as the product of the action of an excess of bromine on beta-naphthol is a mixture of the tri- and tetra-bromo-derivative, which are separated only with difficulty, this observation affords a welcome method of preparing tetra-bromo-beta-naphthol. The readiness with which bromine, in presence of muriatic acid, displaces the sulphonic radicle from the acid, but not from the salt, is calculated to excite surprise.

QUANTITATIVE ANALYSIS BY ELECTROLYSIS.

By ALEX. CLASSEN.

Electrolytic Determination of Lead.

The separation of lead as peroxide requires, as it is well known, the exact observance of certain conditions. According to the statements of Luckow, a certain quantity of nitric acid is required for the complete oxidation to peroxide. The quantity is regulated—as was first ascertained in the electro-chemical laboratory of the Munich Technical High School—by the temperature of the liquid and the density of the current to be used. Concerning the latter point, it was established that it depends on the nature of the anode. If its surface is very smooth it must be only 0·05 ampére (for a surface of 100 square c.m.) or otherwise 0·5 ampére. Even on observing these conditions the quantity of lead which can be deposited as firmly-adherent peroxide is relatively very trifling. The rapid separation of larger quantities of lead peroxide adhering completely like a metal succeeds only if the platinum capsule serving as an anode is roughened internally by means of a sand-blast. On using such capsules it is possible in a few hours to deposit quantities of lead peroxide up to 4 grms. upon a surface of 100 square c.m. with a current of 1·5 ampére. In carrying out the determination of lead we add, after dissolving the lead salt, 20 c.c. of nitric acid (of specific gravity 1·35 to 1·38), diluting with water to about 100 c.c., heating to 50° to 60°, and electrolysing with a current of $N.D._{100}=1·5$ to 1·7 ampére. If the application of heat is continued, the precipitation for quantities of 1·5 grm. lead peroxide is completed in three hours; for larger quantities in four to five hours. We ascertain the completion of the separation, we add about 20 c.c. of water, and observe if any blackening takes place on the surface of the electrode where recently moistened. If blackening is not observed in ten to fifteen minutes, the deposit, after interrupting the current, is washed with water and alcohol, and dried at 180°—190°. The residue is anhydrous peroxide. The tension of the source of the current does not affect the nature of the lead peroxide. In the author's experiments it varied from 4 to 8 volts.

If it is required to determine lead and copper when jointly present, we dilute the solution (made up only to 75 c.c. and containing 20 c.c. of nitric acid), electrolyse the hot liquid with a current of 1·1 to 1·2 ampére (correspondiug to $N.D._{100}=1·5$—1·7 ampére), and interrupt the electrolysis after an hour. The maximum quantity of lead present (98—99 per cent if the lead in solution reaches 0·5 grm.) is then separated as peroxide, whilst the kathode still shows no trace of copper. We then interrupt the current, transfer the liquid into another tared capsule, wash the lead peroxide with water which is added to the copper solution, and determine its weight after drying. For the electric deposition of copper we add to the solution ammonia until the well-known deep blue copper solution appears, and add about 5 c.c. nitric acid. The platinum capsule is then connected to the negative pole of the source of current, and used as an anode to receive the residue of lead peroxide and the perforated electrode of sheet platinum, also rendered mat, the weight of which must be previously ascertained. The liquid diluted to 120—150 c.c. is allowed to become completely cold, and electrolysed with a current of $N.D._{100}=$ 1 to 1·2 ampére. In three or four hours the copper (if not exceeding 0·25 grm.) and the residue of the lead are separated.

The modification of this process, especially important for technical purposes, permits not merely of a far more rapid execution (four to five hours instead of fourteen hours and upwards), but effects an accurate and quantitative separation of both metals, whatever may be their proportions.

On applying this method for the analysis of sulphuretted products, the lead sulphate formed by oxidation makes itself unpleasantly prominent. Its solution in nitric acid, according to its compactness, often consumes more time than the analysis itself.

If lead sulphate has been formed, whether in consequence of oxidation or by the double decomposition of lead nitrate and copper sulphate, we first add ammonia in slight excess and heat for a few minutes. Hereby the dense lead sulphate is converted into loose lead hydroxide. This liquid is gradually poured into the platinum capsule which contains about 20 c.c. hot nitric acid, stirring constantly with the electrode. The residual lead sulphate dissolves either at once (according to its quantity) or in the chief part, so that the remainder dissolves on heating for a short time.

The vessel in which the transformation with ammonia was effected is cleaned first with a little nitric acid and then with water.

The modification above described renders possible the separation of large quantities of manganese peroxide, as also the precipitation of some metals which, *e.g.*, antimony, could hitherto be deposited in small quantities only. The accurate and rapid separation of peroxides in quantity is also valuable for separating them from other metals.

On these experiments, as well as on other improvements in electrolysis, the author purposes reporting in concert with Dr. Piloty, of the Laboratory of Berlin University.—*Berichte der Deutschen Chem. Gesellschaft*, xxvii., 163.

ACTION OF SULPHURIC ACID UPON WOOD-CHARCOAL.

By A. VERNEUIL.

The secondary reactions which accompany the formation of sulphurous and carbonic anhydrides in the reaction of sulphuric acid upon wood-charcoal do not appear to have been hitherto the object of any study.*

The black, viscid, and non-crystalline product which forms the residue of this operation contains several interesting substances, among which I have already been able to extract, in considerable quantities, two of the principal benzene-carbonic acids, mellic acid (pheno-hexamethyloïc acid) and benzene-pentacarbonic acid (pheno-pentamethyloïc acid). Their preparation and identification form the object of this memoir.

* M. Terreil has certainly indicated the formation of a small quantity of an organic acid which sublimes during the preparation of sulphurous acid gas by this process (*Bull. Soc. Chimique*, 2nd Series vol. ii., p. 413).

1. The formation of these acids seems to me principally connected with the great concentration of the sulphuric acid, and consequently with the temperature of the reaction. Hence it is suitable to effect a rapid escape of the gases to prevent, as far as possible, the reflux into the flask of the water produced during the reaction.

On account of the impurities of charcoal (water, ash, &c.), and to avoid the destruction of the products first formed, by a large excess of sulphuric acid, I used in my first experiments only 1400 grms. ordinary acid to 100 grms. charcoal.

A thermometer immersed in the liquid shows that the reaction reaches its full intensity about 280°. The temperature rises to 300° only at the end of the operation. The flask is weighed from time to time, and when it only contains from 90 to 100 grms. of matter, which ensues after heating for about six hours, the process is terminated. It is difficult to exceed these limits without the risk of burning the product. The quantity of organic matter which is carried away with the water and the sulphuric and sulphurous acids which distil over is unimportant. When cold the mass is taken up with water which becomes charged with substances of a deep brown colour, and leaves a black insoluble matter undissolved, in which no trace of the original charcoal can be recognised. This product, which is soluble in alkalis and in concentrated sulphuric acid, will be the subject of future study.

The sulphuric acid contained in the liquid is eliminated by means of barium chloride, avoiding excess. The clear decanted liquid is then evaporated to dryness. There remains a brown amorphous substance, very acid, the weight of which is about one-fifth of the charcoal originally used. This acid mixture is taken up in water and saturated with ammonia, which precipitates the oxides of iron and manganese, the lime, &c., in the state of basic salts. The filtrate, on strong concentration, deposits crystals of ammonium mellate, which are obtained perfectly pure on three or four re-crystallisations from 1½ parts of water. The yield is about 4 per cent of the weight of charcoal originally taken.

This ammonium mellate is characterised by its crystalline form, which, according to Wyrouboff, is that of an orthorhombic prism, with m.m. = 114° 25', $a'\dot{p}$ = 151°, $e'\dot{p}$ = 160·5° similar to that described by G. Rose.

The determination of the ammonia, calculated as NH_4, gives 17·39 per cent. Theory for $C_6(CO_2)_6(NH_4)_6 9H_2O$, requires 17·82 per cent.

With barium chloride it gives in a dilute solution a white amorphous precipitate, which is quickly transformed into a mass of fine characteristic needles which after desiccation over sulphuric acid correspond to the formula $C_{12}O_{12}Ba_3 6H_2O$.

I have found that this ammonium mellate is transformed at 160° into euchroïc acid, which, on a zinc plate, gives the fine characteristic blue colour, turning crimson, on treatment with alkalis (Woehler).

These facts prove that one of the acids produced in the oxidation of charcoal by means of sulphuric acid is mellic acid.

2. I have not found a simple and rapid method for purifying the salts which remain in the brown aqueous solution separated from the crude mellate. The process which I have adopted consists in transforming these ammonium salts into barium salts, in dissolving the latter in hydrochloric acid, then in fractionating the baryta. The brown substances which contaminate these products are thus entirely removed.

To this end the solution of the ammonium salts is evaporated to dryness in presence of a slight excess of barium hydroxide. The basic salts obtained are then dissolved in the cold in HCl diluted with ten parts of water. To this liquid is added a hot concentrated solution of baryta until the formation of a permanent precipitate. After this the precipitation is fractionated by adding to the liquid a solution of 30 grms. barium hydroxide per kilo. of charcoal used.

The first precipitate, separated the next day from the supernatant liquid, carries down with it the chief part of the brown products. On continuing this fractionation until the liquid becomes alkaline, we obtain five precipitates less and less deeply coloured. The two first are crystalline, the three latter gelatinous.

Leaving for the present the three last amorphous precipitates, as well as the barium salt which remains in solution in the ultimate alkaline liquid, I will merely now examine the two crystalline precipitates, which are similar enough to be united together.

They give, in dilute HCl a brown solution, which on concentration deposits an acid barium salt crystallised in needles mixed with barium chloride. These two salts are easily separated from the brown products, and they are obtained quite white after three or four re-crystallisations in dilute HCl. They are then decomposed by an equivalent quantity of sulphuric acid. The barium sulphate is filtered off, the liquid evaporated to dryness to expel hydrochloric acid, and the residue, on a final crystallisation from water, yields pure pheno-pentamethyloïc acid. The yield is 3 per cent of the weight of the charcoal used. This acid, first obtained by Friedel in 1880, by oxidising pentamethylbenzene by means of potassium permanganate is very soluble in hot water, from which it is deposited in fine silky needles. It is soluble in alcohol and ether; it effloresces in the air, and loses 27·56 per cent of water over sulphuric acid. The quantity of water calculated for $C_6H(CO_2H)_5 6H_2O$ reaches 26·60 per cent.

If dried at 110° it agrees with the formula $C_6H(CO_2H)_5$. On saturation with ammonia it precipitates barium chloride; like the corresponding mellate, the amorphous precipitate is not spontaneously converted into crystals. Its alkaline salts give, with silver nitrate, a precipitate which on desiccation contains 64·38 per cent of silver. This salt deflagrates if heated, yielding a black voluminous pulverulent matter, which on roasting leaves a moss of pure silver.

This acid requires for saturation 93·46 per cent KOH. These data suffice to characterise pheno-pentamethyloïc acid.

To complete this investigation it remains for me to purify the fractionation baryta products, which I have not yet been able to examine, and to determine if the acids just described are really derived from carbon, or if they are merely the results of hydrogen products which an incomplete calcination always leaves in wood-charcoal.—*Comptes Rendus*, cxviii., p. 195.

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

SECOND PAPER: THE ANALYSIS OF BARIC CHLORIDE.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 66.)

Preparation of Materials.

Baric Chloride. — The ready crystallisation of baric chloride upon the addition of alcohol to a strong aqueous solution of the salt furnishes an admirable method for the preparation of baric chloride in a pure state. This method of crystallisation was freely resorted to in preparing the pure salt used in the preliminary experiments; but the details of the preparation need not be dwelt upon. The spectroscopic test of the purity of the salt has already been described at length (*Proc. Amer. Acad. Arts Sci.*, xxviii., 7). The purest specimens of baric chloride used in the final experiments were prepared by three methods. According to the first of these methods, after the salt had

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences.*

been crystallised two or three times from water, it was precipitated five times in succession by the addition of strong pure hydrochloric acid to its concentrated aqueous solution. Each time the mother-liquor was wholly discarded, and the crystals were carefully drained. The last precipitate was then dissolved in water, and re-precipitated twice successively by means of the purest alcohol. These and the subsequent operations were conducted in platinum vessels. A portion of the salt thus formed (I.*a*) was used for analyses 22, 25, 31, and 32. The remainder of the crystalline powder was washed four times with pure alcohol on the filter-pump, dried, ignited, and fused in a large platinum crucible. The translucent cake of anhydrous baric chloride was dissolved in the purest water, and the solution was allowed to stand until it had become neutral. After having been filtered from the baric carbonate, which was of a faintly brownish tinge because of the presence of impurity taken from the platinum during the fusion, the baric chloride was precipitated twice more by means of alcohol. The last crystals were dissolved in the purest boiling water, re-crystallised by cooling, and finally washed once with cold water. The very pure salt thus formed was used for Analyses 20, 21, 33, and 35 (Sample I.*c*). The last mother-liquor was freed from most of its salt by the addition of pure alcohol; and the very small amount of salt remaining in solution was recovered by the evaporation of the large volume of alcoholic solution and analysed (Sample I.*b*, Analysis 34).

The second chief specimen of baric chloride was treated in a different way. A large quantity of the commercially pure salt ("purissimum") was dissolved in water, and was then evaporated nearly to dryness with excess of pure hydrochloric acid on a steam-bath, to decompose the thiosulphuric acid which is usually present. The hot dilute solution of the residue was treated with an excess of hydrogen sulphide, and the whole allowed to stand in the dark for a long time in a tightly-corked stout flask. The clear supernatant liquid was syphoned off from the trace of precipitate and made alkaline with baric hydroxide which had been re-crystallised six times (*Proc. Amer. Acad. Arts Sci.*, xxviii., 19). After a suitable time the clear liquid was again decanted and filtered from the sulphides insoluble in the alkaline solution, and all the sulphur from the filtrate was expelled by boiling with hydrochloric acid. The resulting solution was, of course, free from the heavy metals, but it contained marked traces of calcium, strontium, sodium, potassium, and possibly magnesium. After two successive crystallisations from water the salt was still found to contain very small amounts of these metals, but after two precipitations by alcohol the spectroscope was unable to show any impurity in it except a trace of the ever-present sodium, upon very careful testing. The 200 grms. of pure salt thus obtained were then ignited in small portions at a dull red heat. The residue was dissolved in a platinum dish and crystallised, and the crystals were dissolved in pure water. After filtration the solution was acidified by hydrochloric acid and again brought to crystallisation. A portion of the salt thus formed (Sample II.*a*) was used for Analyses 19, 26, 30, and 36, while the remainder was again ignited in platinum, and was re-crystallised twice more after filtration and very faint acidification with hydrochloric acid. The last mother-liquor was evaporated to dryness in platinum, and served for Analyses 23, 27, and 37 (II.*b*). The purest crystals were partly dried over a steam-bath, powdered in an agate mortar, and exposed to a moist atmosphere until constant in weight. These crystals (Sample II.*c*) served for Analyses 28, 29, 38, 39, 40, and 41). An essentially similar preparation, containing somewhat more occluded water, was used for Analyses 42 and 43.

A third sample of baric chloride was prepared from a part of the carbonate used for the preparation of baric bromide, and hydrochloric acid which had been distilled twice in platinum. This was purified in the usual fashion, and served for Analysis 24.

These preparations each gave every evidence of being pure. After most careful fractional separation of the greater part of the barium no trace of calcium or strontium could be found, even in large samples, by means of the spectroscope. The trace of sodium visible undoubtedly crept in during the fractional treatment used to prepare the specimen for spectroscopic examination, for the salt itself before the fractionation showed no more sodium than the surrounding air. The effort was made wholly to free the salt from silica by means of repeated ignition and solution, and the use of platinum vessels; but no proof can be given that it did not contain one or two parts in a hundred thousand of this impurity. The quantitative comparison of these preparations which is made further on, furnished conclusive proof of their similarity, at any rate. If the results are reduced to the basis of 100,000 parts of argentic chloride, and arranged according to the sample of baric chloride used, the following averages are obtained:*—

Preparation.	Experiments.	Parts of baric chloride corresponding to 100,000 parts of argentic chloride.
I.*a*	22, 25	72·649
I.*c*	20, 21, 35	72·651
II.*a*	26, 36	72·668
II.*b*	23, 27, 37	72·650
II.*c*	28, 29, 38, 39, 40, 41, 42, 43	72·657
III.	24	72·650
	Total average..	72·654

It may be remarked that the purest specimen (Preparation II.*c*) gave an average result which is very close to the average of all the specimens.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 1st, 1894.

Dr. Armstrong, President, in the Chair.

Certificates were read for the first time in favour of Messrs. F. E. Allhusen, Jesus College, Cambridge; Charles Henry Ashdown, Belmont, St. Albans, Herts.; Harry Bowes, 9, Union Terrace, Chatham Hill; Thomas Chambers, Dudley House. Coatbridge, N.B.; Edwin Terry, 41, Nightingale Lane, Balham, S.W.; Arthur Robert Golden, B.A., 17, Trinity Street, Norwich; William Albert Knight, Sexey's Trade School, Bruton, Somerset; James Mansell, B.A., 49, Upper Tichborne Street; Charles McMullan, Holywood, co. Down, Ireland; Frederick Wallace Stoddart, Grafton Lodge, Sneyd Park, Bristol; Henry L. Wheeler, 1812, Prairie, Chicago, U.S.A.

Of the following papers those marked * were read:—

*108. "*Note on the Liberation of Chlorine during the Heating of a Mixture of Potassic Chlorate and Manganic Peroxide.*" By Herbert McLeod, F.R.S.

In 1889 the author suggested an explanation of the catalytic action which takes place when an "oxygen mixture" is heated, an essential feature in the explanation being the evolution of a small quantity of chlorine;

* From these determinations all those made according to Stas's first and second methods have been omitted, since these methods proved to be unsatisfactory. Hence Preparatton I.*b* is not represented in the table. The high result from Sample II.*a* (Experiments 26 and 36 are parts of the same analysis) was due to a slight mechanical error.

a few months later O. Brunck published in the *Berichte* a statement that the gas evolved together with oxygen is not chlorine but ozone.

The author has made several experiments to endeavour to solve the question. A mixture of potassic chlorate and manganic peroxide was heated in a test-tube by means of the vapour of boiling mercury, and the evolved gas was passed through a U-tube filled with small glass beads to remove any potassic chloride carried over mechanically, and then through another U-tube containing an ammoniacal solution of argentic nitrate. On subsequently acidifying the solution with nitric acid, argentic chloride was precipitated. The quantity of chlorine calculated from the amount of the precipitate was not dissimilar from the quantity given in the previous paper.

On extracting the residue with water, filtering and adding litmus solution, the liquid was found to be slightly alkaline. The alkalinity was determined by means of a centinormal solution of oxalic acid, and was found to correspond fairly well with the quantity of chlorine in the argentic chloride.

One test only was made for the presence of ozone in the gas. The beads in the first U-tube were moistened with a strong solution of potassic iodide, the mixture was heated as before in mercury vapour, and no colouration was seen on acidifying the potassic iodide solution, indicating that under the conditions of the experiment, ozone was not produced.

DISCUSSION.

Professor DUNSTAN remarked that the odour of the gas evolved from the mixture was more like an oxide of chlorine than chlorine itself. He enquired whether Professor McLeod had ascertained whether a mixture of potassium chloride and manganic oxide furnished chlorine when heated in mercury vapour. If so, then not only the production of chlorine, but also of permanganate and alkali, from the chlorate was susceptible of another explanation.

Professor MCLEOD stated that he had not hitherto closely investigated this question.

109. "*The Examination of some Recent Freezing-Point Determinations.*" By S. U. PICKERING, F.R.S.

Mr. Harry Jones has recently made a number of freezing-point determinations with weak solutions for which a very high degree of accuracy is claimed, and which have led him to the unexpected conclusion that non-electrolytes exhibit abnormally large depressions of a character similar to those exhibited by electrolytes. This must necessarily invalidate all the conclusions drawn from the abnormal depressions given by the latter. On examining his results, it was found that they all formed figures of a curvilinear character, even in cases where the author's previous determinations showed comparative regularity and constancy. It was considered probable that this peculiarity of Mr. Jones's results might be due to some error in the calibration of his instrument, and this was borne out by the fact that the difference between his and the author's determinations were in every case—there being eight cases available for the comparison—of the same sign at the same temperatures, these differences forming, when plotted, a wavy curve. As the author used two different thermometers in his determinations, the error can scarcely be attributed to his instruments. A further comparison with one series of results by Raoult and six series by Loomis, gave confirmatory evidence of the existence of an error of this wavy character in Mr. Jones's results; as also did a comparison of his values with those calculated from Kohlrausch's conductivity determination.

The total error in Mr. Jones's results amounts to at least 0·01°, and is quite sufficient to account for the abnormal results which he has obtained with non-electrolytes, and for the wavy character of his results generally.

His results give clear indications of the existence of changes of curvature in many cases, which would not appear to be negatived by the error of his measurements. In the case of sulphuric acid the peculiar character of the figure which his results form confirms in a striking manner the author's previous results (*Trans.*, 1890, 357), since they show breaks at the same points as the author's did, and the two figures are practically identical when Mr. Jones's results are corrected according to a mean deduced from the comparison with the various authorities mentioned.

110. "*Salts of Dehydracetic Acid.*" By J. NORMAN COLLIE, Ph.D., and H. R. LE SUEUR, B.Sc.

The reason for preparing these salts was, if possible, to obtain additional evidence bearing on the constitution of dehydracetic acid. During many years this substance was considered to be a true acid, that is to say, it was supposed to contain a carboxyl group. Owing, however, to one fact, first noticed by Ostwald, namely, the extremely low dissociation constant, this idea was abandoned, and Feist first suggested that the substance was a lactone.

Naturally, therefore, if dehydracetic acid were a lactone of the formula $C_8H_8O_4$, its salts should possess the general formula $C_8H_9O_5M$; and the examination of these compounds ought to at once decide the question. The salts prepared are the following:—Sodium salt, $C_8H_9O_5Na\cdot H_2O$. Potassium salt, $C_8H_9O_5K\cdot H_2O$. Magnesium salt, $(C_8H_9O_5)_2Mg\cdot\frac{1}{2}H_2O$. Calcium salt, $(C_8H_7O_4)Ca\cdot H_2O$. Barium salt, $(C_8H_9O_5)_2Ba$. Zinc salt, $(C_8H_9O_5)_2Zn$. Cadmium salt, $(C_8H_9O_5)_2Cd$. Cobalt salt, $(C_8H_9O_5)_2Cd\cdot\frac{1}{2}H_2O$. Manganese salt, $(C_8H_9O_5)_2Mn$. Copper salt, $(C_8H_7O_4)_2Cu$. Silver salt, $C_8H_9O_5Ag$. Lead salt, $(C_8H_9O_5)_2Pb$. Ethylic salt, $C_8H_7O_4C_2H_5$.

Nearly all of these were perfectly stable at 100°, but all of them (with the exception of the copper salt and the ethylic salt, which did not lose water) when heated to as high as 145°, gave off water and left, without exception, salts of the formula $C_8H_7O_4M$.

The examination of the salts, therefore, has not enabled the authors to decide the question; for, although all the salts lose water when heated, leaving compounds which are derivatives of the substance $C_8H_8O_4$; still, owing to the high temperature necessary in some cases to effect this change, the water may be other than that of crystallisation.

111. "*A New Method of Producing Carbon Tetrabromide.*" By J. NORMAN COLLIE, Ph.D.

Whilst working with a yellow naphthalene compound which he had obtained from dehydracetic acid (*Trans.*, 1893, 329), the author noticed that when it was heated with a strong solution of sodium hypobromite, it yielded a volatile solid compound. This substance was found to be tetrabromide of carbon and was formed to the extent of about 2—3 grms. from 10 grms. of the naphthalene derivative.

On experimenting with other compounds, the author finds that this interaction is very general, and that widely diverse carbon derivatives all yield tetrabromide of carbon when warmed with strong solution of sodium hypobromite.

Amongst others, may be mentioned alcohol, glycol, glycerol, mannitol, malic acid, citric acid, maleic and fumaric acids, sugars, starches, celluloses, &c. Amongst benzene derivatives, the phenols, especially carbolic acid, orcinol, resorcinol, α- and β-naphthol, alizarin, &c.; oxypyridine derivatives give it easily, also a large number of the alkaloids. It is evidently a very general interaction and depends to a large extent on the powerful oxidising or breaking down power of the alkaline solution of sodium hypobromite. Bromoform is probably formed prior to the final stage which the author is inclined to believe involves the conversion of bromoform into carbon tetrabromide.

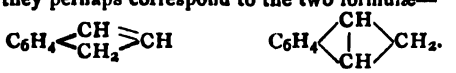
112. "*Metallic Derivatives of Acetylene. Mercuric Acetylide.*" By M. TRAVERS, B.Sc., and R. T. PLIMPTON, Ph.D.

Berthelot (*Ann. Chim. Phys.*, [4], ix., 386), by passing acetylene through a solution of mercuric iodide in potassium iodide made alkaline with ammonia, obtained an explosive mercury acetylide, of which, however, he seems to have made no analysis. The authors have prepared this substance in various ways and studied its composition and properties. They have prepared it by the action of acetylene (1) on freshly precipitated mercuric oxide; (2) on solutions of mercuric cyanide mixed with ammonia, or, better, with ammonia and cupric sulphate or zinc chloride; (3) on solutions of mercuric acetate or sulphate with ammonia, when a part only of the mercury is precipitated; (4) on mercuric oxide dissolved by the aid of ammonia and ammonic carbonate. The latter method is the most convenient. The heavy white powder which separates is well washed and dried at 100°. Analysis gave as the mean of four determinations: mercury, 87·1; carbon, 10·1 and 10·3. Calculated for $3C_2HgH_2O$: mercury, 87; carbon, 10·4 per cent. The substance could not be obtained free from water even after long drying at 100°. Mercuric acetylide belongs to the same class of bodies as the silver and copper acetylides; it is explosive, yields part of its carbon as acetylene when warmed with chlorhydric acid, and part as aldehyd, and yields the compound C_2I_2 and eventually C_2I_4 when acted on by iodine dissolved in potassium iodide. It differs altogether from the substance obtained from solutions of mercuric acetate described in a previous note (*Proc. Chem. Soc.*, 1892, 109), and which is non-explosive and in other respects resembles the allyene derivatives obtained by Katscheroff from solutions of mercuric chloride and acetate (*Ber.*, xvii., 13). Mercuric acetylide detonates violently when suddenly heated or struck sharply; it can, however, be handled with safety even when dry.

Dr. E. H. Keiser, who had apparently overlooked Berthelot's description of the substance and the note published in the *Proc. Chem. Soc.* by one of the authors, has recently (*Amer. Chem. Journ.*, November, 1893) obtained the same substance, and attributes to it the formula C_2Hg: the authors have not been able to obtain either this or the silver compound free from water.

113. "*Synthesis of Indene, Hydrindene, and some of their Derivatives.*" By W. H. Perkin, jun., F.R.S., and E. Révay, Ph.D.

It is shown that when the barium salt of the hydrindenecarboxylic acid prepared by v. Baeyer and W. H. Perkin, jun., is heated, either alone or with sodium methoxide, it yields indene and not hydrindene. The indene thus obtained has a somewhat lower density but somewhat higher refractive and magnetic rotatory power than the indene separated from coal tar, although they are not chemically distinguishable. The authors incline to the view that the two products are isomeric, and that they perhaps correspond to the two formulæ—



The action of bromine on hydrindenecarboxylic acid, and a number of ketones and their derivatives prepared from this acid, are described.

Purification of Rivers.—Dr. Th. Bokorny contributes to the *Chemiker Zeitung* an exhaustive memoir on this important sanitary question. He concludes with this most valuable and unquestionable dictum:—"If we consider that 10 grms. of algæ consume in ten days about 0·1 grm., or daily 0·01 grm., of organic matter, we can form an approximate conception to what extent the—often copious—vegetation of our rivers and brooks purifies the water from organic substances. How many thousand kilos. of water-plants grow in our rivers; how finely divided is this vast mass of assimilating vegetable tissue; how efficacious is the contact between the impure water and the assimilating cells. In truth, we can scarcely conceive of a better agent for the purification of rivers than aquatic vegetation."

NOTICES OF BOOKS.

Quantitative Chemical Analysis. Adapted for Use in the Laboratories of Colleges and Schools. By Frank Clowes, D.Sc., F.I.C., and J. B. Coleman, F.I.C., Assoc. Royal Col. Sci. Second Edition. Small 8vo, 472 pp. London: J. and A. Churchill.

This work, as a whole, merits our hearty approval. Not only are the instructions for analytical operations accurate and clearly described, but there is a careful indication of the needful precautions and niceties. There is no reference to any syllabus or any examination for which the student is supposed to be preparing—not to use a briefer but shorter expression. Theoretical disquisitions have been avoided. The methods laid down are those only which have approved themselves in actual practice, and have been repeatedly used under the author's inspection by the students in Nottingham University College. The bibliographical notes will prove exceedingly useful to those who may wish for further details.

The work is divided into five parts. Section I. treats of preliminary operations and manipulations. Section II. expounds the simpler and more important gravimetric determinations, arranged in the order of increasing difficulty. Section III. gives an account of volumetric determinations, with the preparatory operations. Section IV. introduces the student to more complex determinations, including the analysis of ores, industrial products, water, foods, &c. Lastly, in Section V. we have gas analysis, a subject of constantly increasing importance.

An appendix gives tables of constants, lists of apparatus and reagents required, &c.

The work occupies a happy medium position between the bulky and costly works which the expert has frequently to consult and the bold epitomes with which, of late years, we have been almost smothered.

London County Council. Reports on Sewer Air Investigations. By J. Parry Laws, F.I.C. Ordered to be Printed by the Main Drainage Committee.

The author's experiments, which have evidently been conducted very fairly and carefully, lead to conclusions not quite in harmony with prevalent views on sewage gases and their possible dangers to health. The results are summed up as follows (p. 4):—

I. The micro-organisms in the sewer air are related to the micro-organisms of the air outside, and not to the micro-organisms of the sewage.

II. In the air, both within and without the sewer, the forms of micro-organisms present are almost exclusively moulds and micrococci; on the contrary, the micro-organisms of sewage are for the most part bacilli. Of the latter, sometimes as many as 25 per cent very rapidly liquefy the gelatin on which they grow, whereas in the whole course of my experiments with fresh air and sewer air I only met with one colony—and that a micrococcus—rapidly liquefying gelatin.

III. That for purposes of deodorising, manganate of soda and sulphuric acid and carbolic acid are decidedly the most efficient of the several chemicals tried, and setting aside the question of relative cost, the former is decidedly preferable for the reason stated above.

The author calls attention to the circumstance that his observations hold good only for sewers which convey a large and permanent flow of sewage. What the condition of the sewer air may be where the flow of sewage is intermittent, or in which it stagnates and putrefies, must, he very rightly thinks, be shown by further experimentation.

Some experiments in this direction have accordingly been undertaken (p. 9), with the result that the number of micro-organisms in the air of such sewers considerably exceeds the number in the external air. This excess is,

however, of the less importance, as it relates to moulds and not to bacteria.

The final conclusion submitted is that the organisms of sewer air probably are not a source of danger. Still there is evidence that sewage gas "in some instances has had some causal relation to zymotic disease." He therefore suggests that sewage gases may contain some intensely poisonous chemical substance.

The question may be asked whether in the face of these results the ventilation of sewers is not reduced to a very subordinate rank in hygienic importance?

Extracts from "Micrographia." By Robert Hooke, F.R.S. (Alembic Club Reprints, No. 5). Edinburgh: W. F. Clay. London: Simpkin, Marshall, and Co., Lim. 1894.

This volume consists of extracts from Hooke's "Micrographia," a very curious work published in 1665, in the early days of the Royal Society. The "Micrographia" bears the sub-title "Physiological Descriptions of Minute Bodies made by Magnifying Glasses." It must here be kept in mind that the term physiology was in Hooke's time not restricted to an account of the functions of living organisms, but included a general account of nature, organic and inorganic. The author suggests that as our sense of sight has been enlarged by means of the telescope and the microscope, so the operations of our other senses may be advanced. His "otoconsticon" has been fully realised in the telephone and the microphone, but for the sense of smell on which he expatiates at some length nothing has yet been accomplished.

"Observation XVI." (p. 39) is entitled "Of Charcoal or Burnt Wood," and conveys the author's views on the theory of combustion. He finds that there is "no such thing as an element of fire," and that flame is "a mixture of air and the combustible volatile parts of any body." He rejects the hypothesis of Francisco Stelluto that lignite is clay or earth turned into wood, and maintains that it is vegetable matter in course of conversion into coal.

Hooke, it must be admitted, is stronger in suggestion than in demonstration, but we see that not a few of his hints have not yet been carried into practical execution.

An Epitome of the Law and Practice connected with Patents for Inventions, with a Reprint of the Patents Acts of 1883, 1885, 1886, *and* 1888, *and the Official Rules and a Summary of Foreign and Colonial Patent Laws.* By James Johnson, Barrister-at-Law, and J. H. Johnson, C.E., Solicitor. Second Edition, carefully revised. London: Longmans, Green, and Co., and Stevens and Sons (Lim.). 1894.

This epitome of patent-law is compact, intelligible, and comprehensive. Its only defect is that it simply expounds the law as it is without any attempt to point out what it should be. It is evident that if the two glaring defects of British patent-law—viz., that it is not imperial in its scope, and that it permits aliens to uphold a British patent without working it in the United Kingdom—were mentioned in this and similar publications, the attention of all persons interested would be drawn to the subject. At present the law is in many cases worked, not to introduce new industries into the realm, but to prevent their introduction. In the second place, to obtain protection for an invention throughout her Majesty's dominions involves a heap of formalities and an outlay certainly not far short of £900.

Kelly's London Medical Directory, 1894. London: Kelly and Co., Lim.

This, the sixth issue of the "Medical Directory," has been carefully compiled and, as far as possible, corrected from the previous issues. Not the least important section is the alphabetical list of streets giving the addresses of every medical man in London. We would suggest to the publishers that a great improvement could be made without much extra labour if in the case of "Specialists" their speciality could be mentioned. At present the only indication given of this kind appears to be in the case of dentists.

CORRESPONDENCE.

EXAMINATIONS.

To the Editor of the Chemical News.

Sir,—There is no doubt that both Dr. Tilden and Mr Groves are right. Many students do pass Examinations of the Conjoint Board, of the Universities of London, of Victoria, of the Science and Art Department, and, in fact, all examinations, without a competent knowledge of the subject in which they are examined. But it is impossible to judge satisfactorily of the qualifications of a candidate on the evidence at the disposal of the examiners. And it is impracticable to make the examination so long and exhaustive (and exhausting to examiner and examinee) as to give the examiner any real knowledge of the candidate's ability and attainments, except, perhaps, in examinations for honours, where no syllabus is laid down, and where, owing to the small number of candidates, great attention can be paid to each individual. Not a year passes without my regretting that competent men have failed, while incompetent men have passed examinations of all kinds.

There is one reason why cases such as that of which Dr. Tilden justly complains are so frequent. It is that there is an understanding—an unwritten compact—that no negative marks are to be given. A candidate may make the most egregious blunders in answering one question, such blunders as to show that he really knows nothing whatever of the subject in which he is examined, yet if he produce answers from memory which will pass muster for a sufficient number of other questions, he passes.

Another reason why incompetent men often pass is that that they have, from their youth upwards, been trained in examinational methods. They have learned how to take the measure of an examiner, what form of answer will please him, how much to insert, how much to omit, and how to touch lightly and vaguely on questionable points, so as not to commit himself, and how to make the most of a minimum of knowledge. I well remember the case of a friend of mine who required to pass an examination in tolerably advanced mathematics, and who was a proficient in examinations in classics and metaphysics. With the help of a coach, *in a fortnight*, from such slender knowledge as almost amounted to absolute ignorance, he passed his examination with credit. He is now a successful barrister.

Such training is, indeed, of the greatest service to a barrister. For he has to get up a brief, often on a technical subject, in the minimum time, to display what he knows to the best advantage, and to conceal what he does not know. And it is for this reason, doubtless, that many of our wranglers hold such distinguished positions at the bar.

But such a habit of mind is not merely useless but positively detrimental to the student of science, whether he intends to devote his knowledge to technical arts or to medicine. For he is seldom or never required to make up his mind on the spur of the moment; he has leisure to think over doubtful points, and to consult literature, and, if necessary, to take the advice of his colleagues.

Far, however, from denying the necessity of examina-

tions, I should increase them in number. As often as once a fortnight in lecture subjects is not too often. And in practical subjects every exercise should be an examination. It is only thus that ability can be valuated, and steady continuous work meet with due reward. But, it will be answered, how can this system be carried out? With perfect ease. All the machinery is at hand. There are persons selected to fill important posts because of their intellectual and moral qualities; posts in which they have to instruct youth. These are the very persons who are chosen by Universities and Boards as examiners. But with extraordinary perverseness they are set to examine, not their own students, about whom they know much, but each other's students, about whom they know nothing. Is it imagined that the persons who can be trusted to superintend the education of a number of lads cannot be trusted to examine their own pupils for fear of favouritism? Though I have never known an instance of the kind (to the credit of examiners be it said) it has often occurred to me how easy it would be, by collusion between the examiners from different institutions, to pass their own pupils. But the known moral probity of such men is above suspicion. Why, then, if they are able to withstand such temptation, object to their judgment of the work of their own pupils?

The objection will, of course, be raised:—How is uniformity of standard to be attained? How is uniformity of standard attained in different subjects in, say, the Intermediate Science Examination of the University of London? How can anyone say that the examination in biology is not more difficult or easier than the examination in physics? Here the common sense of the teachers must be the guarantee; and, though complete uniformity is not to be expected, it is probable that in any average class, if the passes amount to fifty per cent of those examined, and if the examination papers bear a general resemblance to each other, the right persons, if examined by their teacher, will have passed. As it is probable that this question will come very much to the front in the evolution of the New University for London, I have thought it advisable to write you at length on the matter; and I would suggest, in case many others share the views which I have stated, that a Committee of teachers be appointed to use every effort to get them carried into effect. They represent the established custom in every country except our own; and it is time that an examinational system, which I take to have been a protest against the favouritism of election to posts in the unreformed civil service, and which, no doubt, did good in its day, should now be completely altered.—I am, &c.,

W. Ramsay.

University College, London.

CHEMISTRY AT THE CONJOINT BOARD.

To the Editor of the Chemical News.

Sir,—I am not prepared to admit Mr. Groves's hypothesis as to a third possible cause of the unsatisfactory position of chemistry at the Conjoint Board, and I shall not allow myself to be drawn into a controversy as to the various modes of conducting examinations. I will content myself with saying that the Examinations of the University of London and of the Science and Art Department are not conducted in the way he describes. I have no personal knowledge of the work at Victoria University, and therefore cannot answer for what is done in Manchester; but if Mr. Groves had had any experience as an examiner he would know that in every properly-conducted examination each case is disposed of according to its merits, and not, as he supposes, according to some rigid scale of marks. Such a system may be adopted at some *competitive* examinations, such as those for admission to the Civil Service, though I should hope that even in these cases the exercise of a little common sense would be permitted. As to the Conjoint Board, whether the rigid mark system is adopted there or not Mr. Groves's hypothesis affords no explanation of such cases as the one I specially referred to in my former letter.—I am, &c.

William A. Tilden.

The Mason College, Birmingham,
February 12, 1894.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

Sir,—It is intended to bring before the annual meeting a proposal to delete from the "Regulations for Admission to Membership," page 8, paragraph 3, the words:—"In any one or more of the Universities, or Chartered or Incorporated Colleges or Schools approved by the Council," and that the further necessary alterations be made in other paragraphs consequent on this change.

May I be allowed to explain that this Regulation enables persons who are not Members of the Institute to allege that it does not admit all properly qualified chemists, but only those who have obtained their training at certain specified places.

It is chiefly for the purpose of strengthening the position of the Institute, when pointing out to public bodies that its members should be regarded as the only fit and proper persons to hold Public Chemical Appointments, that this change is most urgently required, and it is felt that the utility of the Institute will be much restricted and its progress impeded by accepting for examination *only* those Candidates who have studied Mathematics, Chemistry, and Physics in certain specified buildings.

Men will enter the profession through other than the specified channels whatever the Institute may do, and it is clear that the sooner this is recognised the better.

There can be practically no disagreement with the other rules of the charter: that a candidate for Associateship should have a good general education; that he should prove by note-books and otherwise that he has been regularly and well trained in Theoretical and Practical Chemistry, Physics, and Mathematics, besides being called upon to pass the examinations of the Institute, and I think there could be no objection to the standard of education being raised.

In the large majority of cases, the most simple way of obtaining the required education is by attending the courses of studies given at the Universities, Colleges, and Schools specified by the Institute; but this is all the more reason why it is unnecessary to *insist* on Candidates passing through them as a *sine qua non* to their entering the profession.

This proposition will be largely supported, and I am requested to ask if those members who are in favour of the proposed alteration and who have not yet communicated with me, will kindly do so.—I am, &c.

William Thomson,
Hon. Sec. Institute of Chemistry
Reform Association.

Royal Institution Laboratory, Manchester,
February 13, 1894.

Preservation of a Constant Level in Water-baths and for the Extinction of the Flame in a Dried-up Water-bath.—Concerning the former part of the invention no particulars are given. As regards the second portion there is introduced into the gas-pipe a metal cock, the out-flow pipe of which is prolonged for from 10 to 15 c.m., and is loaded at its end with a weight. This rests freely upon one end of a flat piece of iron wedged between the water-bath and the tripod in such a manner that as the bath becomes gradually lighter the iron falls and turns off the gas-cock.—*Chemiker Zeitung.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 5, January 29, 1894.

Synthetic Borneols.—G. Bouchardat and J. Lafont.—The author proposes for each of these isomers a name recalling its origen. Thus we have the borneols of camphene, and of terebenthene, borneol having a reversible power.

Thermic Constants of certain Polyatomic Bases.—Albert Colson and Georges Darzens.—For ethylenediamine, $C_2H_4,2NH_2$, the authors find the specific heat 0·84 between 12° and 45°. At 15° the solution of 1 mol. (*i.e.*, 60 grms.) of ethylenediamine in 4 litres of water evolves 7·6 cal. The mean neutralisation heat determined with hydrochloric acid at ½ mol. per litre is 23·54 cal. The solution heat of 1 mol. of neutral quinine sulphate in 12 litres of acidulated water is −6·7 cal. The neutralisation heat was found +15·5.

Bulletin de la Société Chimique de Paris. Series 3, Vols. xi.-xii., No. 2.

Essence of Tarragon and its Transformation into Anethol.—E. Grimaux.—Estragol and anethol differ by the isomerism of their group C_3H_5.

Chloralose.—M. Hanriot and Ch. Richet.—Chloralose and its derivatives all contain three atoms of chlorine, whence it appears that the group CCl_3 of chloral is found in all the derivatives of chloralose, and that the union of chloral with glucose takes place by its aldehydic group CHO. The aldehydic function of glucose is suppressed.

Nature of the Forces which Intervene in Dyeing.—A. Rosenstiehl.—The forces which co-operate in the operations of dyeing are of two kinds: adhesion or cohesion, which is always in action; it is a manifestation of the attraction of matter for matter. The chemical forces often intervene, but they are not always indispensable in an evident manner. They take their place in the second line. The mechanical theory and the chemical theory as expounded by their partisans are mutually exclusive and in error. They regard only one side of the question. Dyeing may be defined as the operation which consists in covering the textile fibre with a perfectly adhesive layer of a coloured substance, which is often a combination of a part of the substance of the fibre with a colouring matter.

Some of the most Recent Modifications Applied to the Manufacture of Coal-gas.—P. Mallet.—This memoir is too voluminous for useful abstraction.

MISCELLANEOUS.

"Optimus" 100 Guinea Competition.—This is surely an age of prize giving and prize competitions; one can hardly open certain journals without finding prizes offered in a most lavish manner. Most of these, however, are a pure matter of luck, and require no skill whatever. The recent "Optimus" competition promoted by Messrs. Perken, Son, and Rayment was originated by them in 1892; so this, which has just taken place, is the second. They offered seventeen prizes of a total value of £105 for the best photographs of various kinds taken by amateurs only with Messrs. Perken and Co.'s apparatus. The photographs were divided into nine classes, and have resulted in some very excellent work. Some hundreds of pictures having been sent in, the task of adjudication must have been exceedingly heavy, but it speaks well for the popularity of the competition. Judging from the numbers of prizes awarded in the different classes, the favourite subject appears to have been architecture, though some very beautiful landscapes were sent in. Photography has made great strides of late years, the work of many amateurs being now quite equal to, if not better than, that of most professionals, the reason for this probably being that the latter simply look upon photographs as so many shillings earned, while with the former it is more a "labour of love," every picture taken bringing back old scenes and memories when looked upon in after years.

The Royal Society of New South Wales.—*Original Researches.*—The Royal Society of New South Wales offers its medal and £25 for the best communication (provided it be of sufficient merit) containing the results of original research or observation upon each of the following subjects:—

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51.—On the effect of the Australian Climate on the Physical Development of the Australian-born Population.

The competition is in no way confined to Members of the Society, nor to residents in Australia, but is open to all without any restriction whatever, excepting that a Prize will not be awarded to a Member of the Council for the time being; neither will an award be made for a mere compilation, however meritorious in its way. The communication, to be successful, must be either wholly or in part the result of original observation or research on the part of the contributor. The Society is fully sensible that the money value of the Prize will not repay an investigator for the expenditure of his time and labour, but it is hoped that the honour will be regarded as a sufficient inducement and reward. The successful Papers will be published in the Society's Annual Volume. Fifty reprint copies will be furnished to the author free of expense. Competitors are requested to write upon foolscap paper—on one side only. A motto must be used instead of the writer's name, and each Paper must be accompanied by a sealed envelope bearing the motto outside, and containing the writer's name and address inside. All communications to be addressed to the Honorary Secretaries, T. W. E. David and J. H. Maiden, The Society's House, 5, Elizabeth Street, Sydney.

Carmine.—Sigmund Feitler.—The moisture in five samples of pure carmines was respectively 17·00, 15·50, 20·48, 13·15, and 15·69, or on an average 16·36 per cent. The ash ranged from 8·1 to 10·51 per cent, the colouring matter varied from 57·14 to 67·2 per cent. Alumina was present in all the samples, from 25·95 to 43·18 per cent., calculated on the weight of the ash. SnO_2 was present in all and appears to be essential.—*Zeit. Angewandte Chemie.*

MEETINGS FOR THE WEEK.

MONDAY, 19th.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "The Decorative Treatment of Artificial Foliage," by Hugh Stannus, F.R.I.B.A.
TUESDAY, 20th.—Royal Institution, 3. "Locomotion and Fixation in Plants and Animals," by Prof. Charles Stewart, Pres.L.S.
—— Society of Arts, 8. "The Arts and Industries of Belgium and the Antwerp Exhibition, 1894," by Edouard Sève.
—— Institute of Civil Engineers. 8.
—— Pathological, 8.30.
WEDNESDAY, 21st.—Society of Arts, 8. "Electric Signalling Without Wires," by W. H. Preece, F.R.S.
—— Meteorological, 8.
—— Geological, 8.
—— Microscopical, 8.
THURSDAY, 22nd.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "The Past and Future of Mountain Exploration," by W. Martin Conway, M.A., F.R.G.S.
FRIDAY, 23rd.—Royal Institution, 9. "Transformations of Electric Currents," by Prof. Silvanus P. Thompson, D.Sc., F.R.S.
—— Physical, 5. "A Method of Determining Refraction Indices," by Mr. Littlewood. "A New Electrical Theorem," by Thomas H. Blakesley. "The Attachment of Quartz Fibres," by Prof. C. V. Boys.
SATURDAY, 24th.—Royal Institution, 3. "Light, with special reference to the Optical Discoveries of Newton," by the Right Hon. Lord Rayleigh, F.R.S.

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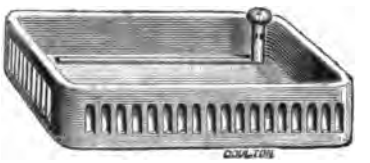

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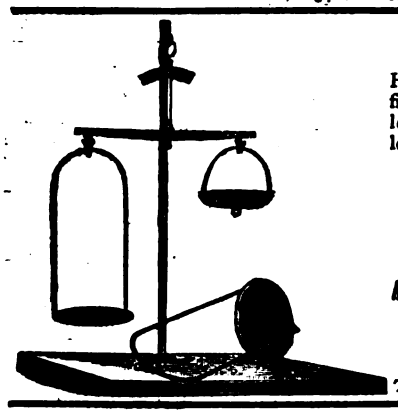

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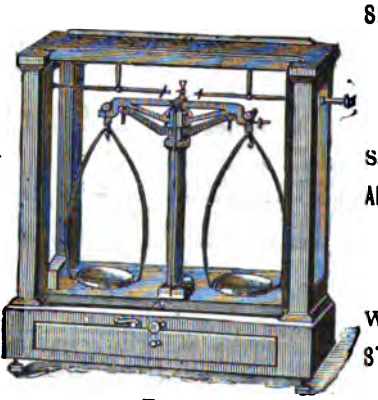

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THE CHEMICAL NEWS.

Vol. LXIX., No. 1787.

THE ACTION OF HEAT UPON ETHYLENE.*

By VIVIAN B. LEWES.

The decompositions of the simpler forms of hydrocarbons at an elevated temperature has always been recognised as a question of the greatest importance, as upon them is dependent a true conception of many of the actions taking place in the manufacture of coal-gas and other kindred processes of destructive distillation.

Ethylene has in most cases been chosen as the hydrocarbon which would lend itself most readily to experimental researches upon this point, as, besides being one of the simplest, it is easily prepared, and is, moreover, found as one of the products in nearly all cases where organic compounds are subjected to distillation at high temperatures.

No sooner had the difference between ethylene and methane been recognised, than experiments were made by Deimann, Van Troostwyk, Lauwerenburg, and Bondt (*Annales de Chimie et de Physique*, 1st Series, xxi., p. 48) to ascertain the action of heat upon the newly-formed compound, and the conclusions which they came to were that on heating no contraction in volume was observed, but that the tubes in which the decomposition was effected became coated with a black deposit, and drops of an oily body were formed, the gas at the same time losing its property of forming an oily liquid with chlorine.

These experiments were afterwards repeated by Fourcroy, Hecht, and Vanquelin (Gilbert's *Annalen*, ii., 210), who showed that when heated, ethylene yields hydrogen with deposition of carbon, whilst in 1805 William Henry (*Nicholson's Journal*, 1805) showed that ethylene was formed during the destructive distillation of organic bodies, and that on further heating the gas, other changes were observed, and the gas was eventually converted into carbon and hydrogen. The deposition of carbon was also noticed later by Quet (*Comptes Rendus*, xlii., 903), who on passing sparks through ethylene found that carbon was deposited, and formed a bridge between the poles used for the discharge, whilst Dalton showed by the continuous action of the electric spark that ethylene yielded double its own volume of hydrogen, carbon being deposited.

Marchand (*Journ. für Prakt. Chem.*, xxvi., 478) came to the conclusion that at a red heat this gas splits up into methane and carbon, but at a white heat into carbon and nearly pure hydrogen, whilst Magnus, in 1847, made the important observation that on leading ethylene through a red-hot tube a contraction in volume followed; the residual gas consisted of methane, hydrogen, and unchanged ethylene, whilst carbon was deposited, and fluid and even solid hydrocarbons were obtained.

In 1860 H. Buff and A. W. Hofmann (*Liebig's Annalen der Chemie*, cxiii., 119) published a paper on the "Dissociation of Gaseous Compounds on Heating by Electricity."

They found that when a platinum spiral is heated by the galvanic current in pure ethylene there is at once a visible separation of carbon, which covers the sides of the tubes with a black deposit, whilst hardly any expansion in the volume of the gas takes place, from which they assume that the ethylene has split up into methane and carbon.

If the action on the gas, due to the incandescent platinum wire, is allowed to continue, then an increased amount of the gas undergoes dissociation, and soon after the separation of carbon commenced, they observed an expansion which is rapid at first, and in ten minutes reaches a maximum. Similar phenomena were noticed with the spark current; at first the spark had a pale reddish tint which gradually turned to violet, immediate separation of carbon taking place, the spark being frequently stopped by scales of carbon which formed a bridge between the poles. They found that under these conditions the volume of gas expands very rapidly at first but afterwards more slowly, and that after twenty to twenty-five minutes the point of maximum expansion is reached, so that 7 c.c. of dry ethylene gave, after decomposition, 12·25 c.c. They noted also that the residual hydrogen had an unpleasant smell, and burnt with a slightly luminous flame.

Berthelot (*Annales de Chimie et de Physique*, 4th Series, xvi., 144), in 1869, claims that ethylene breaks up under the influence of heat into acetylene and hydrogen, as expressed by the equation—

$$C_2H_4 = C_2H_2 + H_2,$$

and shows that the acetylene then polymerises into benzene, styrene, and other liquid products of higher boiling-points. Naphthalene was also formed by the direct condensation of styrene and acetylene. He also points out that during the heating of ethylene a large proportion of ethane was formed, and his final conclusion is that the heating of ethylene results in the splitting up of 2 mols. of ethylene into acetylene and ethane, and that the formation of solid and liquid products is due to the subsequent condensation of the acetylene.

In 1886 (*Am. Chem. Journ.*, viii., 153) Day made a number of experiments in order to determine the lowest point of temperature at which the constitution of ethylene undergoes alteration, and the nature of the changes taking place at that temperature. In order to do this, he devised an ingenious apparatus in which the ethylene could be heated for very long periods in a hard glass tube. From these experiments he concluded that when the action is continued over a long period the gas undergoes change at much lower temperatures than had been previously observed. The alteration in constitution commences at about 350° C., at which temperature the change is one of condensation without the formation of members of any series of hydrocarbons having a percentage of hydrogen and carbon different from ethylene, whilst if ethylene is maintained at 400° for a sufficient length of time, it is entirely decomposed, marsh gas, ethane, and liquid products being obtained.

In the same year, Messrs. Morton and Noyes (*Am. Chem. Journ.*, viii., 362) made an elaborate investigation with the object of determining whether crotonylene, C_4H_4, which is present in small quantities in illuminating gas and other products of the distillation of organic matter, is formed as a primary product of decomposition by heat, or as a secondary product of the action of heat upon ethylene.

Coal-gas was passed slowly through a hard glass tube 15 m.m. in diameter, which was maintained at a low red heat for a distance of 60 c.m. The products issuing from this tube were first passed through a series of U-tubes surrounded by a freezing mixture; the products which were not condensed were passed through an ammoniacal solution of cuprous chloride, to absorb hydrocarbons of the acetylene series, whilst samples of the gases escaping absorption were finally collected over water. Carbon was deposited in the decomposition tube, and at the end of one month 15 c.c. of liquid had been slowly condensed in the U-tubes, and in this liquid they detected bensene, naphthalene, anthracene, and some other aromatic hydrocarbons, present in quantities too small for determination. Faint traces only of precipitate were found in the ammoniacal cuprous chloride solution, whilst among the bodies absorbed by bromine they identified crotonylene tetrabromide, and the gas collected over water proved to be a

* A Paper read before the Royal Society.

mixture of methane and ethane. The absence of acetylene from the products obtained led them to the view that these products are formed directly by the action of heat upon ethylene.

From the work of the earlier observers, the text-books have accepted the equation—

$$1.\quad C_2H_4 = C_2 + 2H_2$$

as representing the decomposition which takes place at a very high temperature; whilst, on the evidence of the work done by Marchand, and Buff and Hofmann, they represent the change taking place at a lower temperature by the equation—

$$2.\quad C_2H_4 = C + CH_4.$$

During my attempts to trace the actions taking place in the inner zone of luminous flames, I was struck by the complexity of the changes, and the absence of any evidence which would tend to confirm the second equation, and I have made the experiments detailed in the following paper in the hope of being able to trace the decomposition effected by heat in such simple hydrocarbons as ethylene, ethane, and methane.

The first step was to make experiments to corroborate the statement made by Day that, if ethylene is heated at 400° C. for a sufficient length of time, it is entirely decomposed, with formation of methane, ethane, and liquid products.

In order to do this, an apparatus of the form used by Day in his experiments was employed, the only difference being that instead of using an air thermometer, the temperature was taken by means of a platinum and platinum-rhodium couple—as introduced by Le Chatelier, and fully described by Mr. C. Roberts-Austen—which had been previously carefully calibrated, employing salts of known fusing-points. The ethylene was prepared for this and for all the following experiments by making a mixture of 25 parts by weight of rectified methylated spirit and 150 parts of strong sulphuric acid. The mixture was heated in a flask containing a layer of sand, and the gas evolved was washed by contact with strong sulphuric acid, and by passage through several bottles containing a strong solution of caustic soda. The gas was stored in a glass gasholder for several days over water containing sodic pyrogallate and sodic hydrate, to absorb all traces of oxygen, and on analysis gave—

Ethylene	98·80
Nitrogen	1·20

The gas was then passed through the combustion tube until it was considered that all air had been displaced, and the tube was maintained for one hundred hours at 400° C. Oil and a very small quantity of carbon deposited in the tube, and the volume decreased from 100 to 61. The gas was then removed from the tube and analysed.

In all the analyses described in this paper, the following procedure was adopted. Carbon dioxide was absorbed by means of a 50 per cent solution of sodic hydrate, the oxygen estimated by absorption with alkaline pyrogallate, the unsaturated hydrocarbons next absorbed by means of a solution of bromine in potassium bromide, care being taken to remove bromine vapour from the gas by agitation with caustic soda before measurement, the carbon monoxide was next estimated by acid cuprous chloride, and after removal of any acid fumes the residual gas was treated with paraffin oil, previously prepared for use by heating it over a water-bath for at least an hour.

Experiments show that in the case of mixtures of methane with higher members of the same group, agitation with paraffin prepared in this way or mere standing in contact with it with occasional agitation for twenty to thirty minutes, will remove the ethane and any higher saturated hydrocarbons which may be present, together with a small proportion of the methane. The amount of residual methane can then be determined by explosion with oxygen, and subsequent estimation of the carbon dioxide formed, the volume of gas absorbed by the paraffin *plus* the volume resulting from explosion giving the total volume of saturated hydrocarbons. Details of the results obtained by this method of procedure when dealing with gaseous mixtures of known composition will be found, *Journ. Chem. Soc. Ind.*, vol. x., p. 407.

The analysis of the heated ethylene gave—

Carbon dioxide		0·82
Oxygen		0·00
Unsaturated hydrocarbons		7·00
Carbon monoxide		1·17
Saturated hydrocarbons—Paraffin .. 40·18 / Explosion 21·64		61·82
Hydrogen		22·18
Nitrogen		7·01
		100·00

the oxides of carbon and increase of the nitrogen showing that some air had remained in the tube.

A second analysis was now made, but instead of estimating the saturated hydrocarbons by first absorbing the higher members and some methane by paraffin, they were exploded with oxygen, and the methane calculated from the carbon dioxide amounted to 112·5 per cent, showing that ethane and probably even higher members of the series were present, results which fully bear out the statement made by Day as to the decomposition of the ethylene taking place at a temperature of 400° C., and also the statements made by Berthelot and by Day, that under the conditions of this experiment ethane or at any rate higher members of the C_nH_{2n+2} series are formed as well as methane.

It would, however, be manifestly wrong to assume that the formation of the higher paraffins was a primary action, as keeping the hydrocarbons formed by the primary changes at a temperature of 400° C. might easily lead to the formation of secondary products by interaction between the gases.

It seemed much more probable that the character of the primary decompositions would be ascertained by rapidly heating the gas, and as rapidly removing the products of decomposition from the influence of heat, and that this would be effected by passing a regular current of the gas through a very narrow tube heated for 140 m.m. to a known temperature.

The necessity for heating this tube to temperatures above 1000° C. practically limited the choice of material of which it could be made to fire-clay or platinum. It was at first feared that the use of the latter might interfere with the changes taking place, but a long series of comparative experiments, in which ethylene was decomposed by passing through (*a*) a pipe-stem glazed with borax, and (*b*) a platinum tube 2 m.m. in diameter, both being heated to the same temperature, showed that the platinum tube was free from experimental objection unless a considerable percentage of oxygen was present, and that, even with a new tube, the decompositions were of the same nature as when the pipe-stem was employed.

Under these conditions the platinum tube possessed so many advantages over the clay pipe that in all the subsequent experiments a platinum tube, 2 m.m. in diameter and about 40 c.m. in length, was used, and, in order to accurately measure the temperature to which the gas in the tube was heated, the following arrangement was devised:—

Ethylene was stored in a gas-holder, and, after passing over calcic chloride to dry it, entered the platinum tube. In this tube the platinum and the platinum-rhodium thermo-couple, was arranged in the following fashion:—

The two wires are twisted together for a length of 3 m.m., and the wires on either side of the twist are then passed through thin glass tubes, which are fused on to them; having been in this way coated with glass so that only the twist is exposed, they are passed through the platinum tube, the glass insulating the wire from the tube,

and also keeping the thermo-junction in such a position that it registers the temperature of the gas in the tube, not that of the wall of the tube.

To each end of the platinum tube glass T-pieces are fitted, down the stems of which the wires pass to mercury seals; from the metal seals conducting wires lead to the resistance coils, the key, and a reflecting galvanometer. The products, after leaving the platinum tube, pass through a U-tube, cooled in ice and salt in order to condense any liquids, and then through a collecting tube, from which the sample of gas for analysis for gas is taken, thence to Volhard absorption flasks (containing ammoniacal silver nitrate for the estimation of acetylene), the flow of the gas through the apparatus being regulated by means of the aspirator bottle.

(To be continued).

ON THE PHOTOGRAPHIC ARC SPECTRUM OF IRON METEORITES.*

By Professor J. NORMAN LOCKYER, C.B., F.R.S.

This communication consists of a discussion of the photographic arc spectra of the Nejed and Obernkirchen meteorites, the wave-lengths of the lines being based upon those determined by means of the photographic arc spectrum of electrolytic iron, a paper concerning which has been recently communicated to the Society. The portion of the spectrum covered by the photographs extends from K to D.

The wave-lengths, intensities, and origins of the lines in the spectra are given in tabular form.

The following general conclusions have been arrived at:—

1. The spectra of the two meteorites closely agree, both as regards the number and intensities of the lines, the slight difference in number being probably due to a difference in number being probably due to a difference of exposure.

2. The meteoritic spectra and the solar spectrum show considerable similarity. The iron lines in each have about the same relative intensity, thus indicating that the temperature of the iron vapour in the sun which produces the majority of the iron lines is about the same as that of the electric arc.

3. The results of the inquiry into the origin of the lines, in addition to those of iron, may be thus summarised:—

Substances certainly present.	Substances probably present.
Manganese.	Strontium.
Cobalt.	Lead.
Nickel.	Lithium.
Chromium.	Cerium.
Titanium.	Molybdenum.
Copper.	Vanadium.
Barium.	Didymium.
Calcium.	Uranium.
Sodium.	Tungsten.
Potassium.	

4. Of the few faint lines in the tables, for which no origins have been found from the Kensington maps of metallic arc spectra, the majority are apparently coincident with lines mapped by Messrs. Kayser and Runge in the iron spectrum. These do not appear in the Kensington photographs, probably on account of insufficient exposure.

5. By noting the difference in intensity of identical lines in the two spectra, a rough approximation can be made to the relative quantities of the different substances present in the meteorites. Thus it is found that the chief chemical difference between the two meteorites is that there is a preponderance of calcium in the Nejed, and of nickel, barium, and strontium in the Obernkirchen, meteorite.

* Abstract of a Paper read before the Royal Society.

CHEMICAL ANALYSIS OF THE METEORIC STONE FOUND AT MAKARIWA, NEAR INVERCARGILL, NEW ZEALAND, IN THE YEAR 1886.*

By L. FLETCHER, M.A., F.R.S.,
Keeper of Minerals in the British Museum.

The results of a microscopic examination of this meteorite by Professor Ulrich have already been published. Mr. Fletcher has now completed the chemical analysis of the stone, and here gives a detailed account of the method and his observations for the convenience of future analysts of such bodies. After pointing out the advantages of various separate processes, the author briefly describes the composite method adopted by him as follows:—

It was found advisable to make a preliminary separation by means of a magnet into attracted and unattracted material. Treatment of the attracted material with a solution of mercuric ammonium chloride, as recommended by Dr. Friedheim, revealed the fact that the proportion of rust was too large to be negligible, and indicated the necessity of a preliminary reduction of the rust of the unattracted material, and of subsequently extracting the reduced metal with mercuric solution; this prevents the unattracted oxide of iron due to rusting of the alloy from passing into the hydrochloric acid extract with the oxide of iron of the silicate decomposed by the acid. Accordingly, after the sulphur and phosphorus of the unattracted material had been determined, mercuric solution was employed both before and after heating the material to low redness in a current of hydrogen (as recommended by Von Baumhauer), the residual unrusted and rusted nickel iron being thus separately removed. Analysis of the post-reduction mercuric extract showed that there had been a small, but appreciable, action on the silicate portion of the stone during the reduction. Further, it became obvious that the troilite was largely affected by the heating in hydrogen, and in such a way that the greater part of the iron of that constituent, and practically all the iron and nickel of the schreibersite, had gone into the mercuric solution. Hence, determinations of the sulphur and phosphorus in the mercurialised residue were made, so that the iron and nickel which had passed into the mercuric solution from the affected troilite and schreibersite might be allowed for. The mercurialised residue was next treated with hydrochloric acid, and the solution analysed; the silica was extracted from the undecomposed residue by sodium carbonate solution containing some caustic soda, and the small amounts of bases simultaneously extracted were likewise determined; the undecomposed residue itself was then separately analysed. Further various determinations of the alkalis were made.

The interest of the investigation is not in the mineralogical results, which add nothing to our knowledge of meteorites, but in the study of a composite method applicable to the most complicated meteoritic chemical analysis, namely, that of a partially rusted meteoric stone.

* Abstract of a Paper read before the Royal Society.

University College Chemical and Physical Society.—The Annual Public Address will be delivered in the Chemical Theatre of University College, Gower Street, by Prof. J. Millar Thompson, F.R.S.E., on Wednesday, February 28. Subject: "Some Phenomena connected with Solution and Crystallisation." Prof. W. Ramsay, F.R.S., will take the Chair at 8 o'clock.

A RECENT POISON CASE.

By WILLIAM P. MASON.

A NUMBER of interesting points, bearing upon the chemico-legal side of arsenical poisoning, having arisen during a recent trial with which the writer was connected as expert, the following is given as a brief report of the case.

The deceased, a farmer, bachelor, sixty-five years of age, and in good health, was taken violently sick shortly after breakfast, with vomiting and distress in the stomach. Although a physician was summoned, the symptoms increased in severity, and a little after midnight death ensued. The funeral took place three days later. Certain very damaging pieces of circumstantial evidence having been collected, the housekeeper was arrested on the charge of murder, it having been shown among other things, that on the day preceding the death she had purchased an ounce of white arsenic.

Thirty-five days after death (from March 20 to April 25) the body was exhumed, and found in a state of remarkable preservation, and free from cadaveric smell. The stomach presented evidences of inflammation.

Those portions sent to this laboratory for examination were the stomach, portion of intestine, portion of liver, one kidney, and the heart. Arsenic was found in all these parts. White octahedral crystals were found in the contents of the stomach, which on separation gave arsenical reaction.

The methods of testing for the arsenic found in the various tissues were the Marsh and Reinsch, with the usual precautions, checks, and modifications.

The arsenic as found was:—

Stomach and intestine	0·2376 grm.
Liver and kidney..	0·0032 ,,
Heart	0·0007 ,,
Total as metallic arsenic	0·2415 ,,

This would correspond to 4·91 grains of white arsenic.

These weighings having been of tube deposits of metallic arsenic derived from the Marsh test, they did not represent all the arsenic present in the tissue, there having been unavoidable loss. Allowance having been made for such loss, the estimated amount of white arsenic present was six grains.

The amount of arsenic recovered and produced in court was, however, in quantity sufficient to produce death. Some time after the analytical report was made to the coroner, it was learned that an embalming fluid, highly arsenical in character, had been used upon the body by the undertaker at the time of preparation for burial. It is important to note that no injection of this embalming fluid was practised, but that cloths wrung out in the fluid were laid upon the face and chest and were kept constantly wet therewith during a period of many hours. In all about two quarts of embalming fluid were so used. Its composition appeared to be a strongly acidified solution of sodium arsenite and zinc sulphate. Only the arsenic and zinc were determined quantitatively, and they were found to be, zinc (metallic) 1·978 per cent and arsenic (metallic) 1·365 per cent by weight. An amount of this fluid measuring 15·7 c.c. would thus contain a weight of arsenic equal to that actually recovered from the body.

Extended medical testimony was offered by the people tending to show that, under the given circumstances, no fluid of any kind could have reached the stomach through the nose or mouth after death, thus anticipating what the defence afterwards claimed, that the undertaker was responsible for the arsenic discovered in the remains.

In order to gather further light upon the possibility of cadaveric imbibition of embalming fluid through the unbroken skin, test was made for zinc in the heart and stomach, and greatly to my surprise distinct traces of the metal were found in each instance. That at least a portion of the arsenic found in the body was due to post mortem causes was thus distinctly proven. A weighed portion (sixty-two grms.) of the stomach and contents was then most carefully analysed quantitatively for both zinc and arsenic with the following results:—Arsenic, 0·0648 grm., and zinc, 0·0079 grm. Bearing in mind the relative quantities of the two metals in the embalming fluid, it will be seen that the arsenic found in the sixty-two grms. of the stomach was nearly twelve times larger than it should have been to have balanced the zinc which was also present. This fact, together with the discovery of crystals of white arsenic in the stomach, constituted the people's case so far as the chemical evidence was concerned.

The defence made an unsuccessful effort to show that the crystals of the tri-oxide originated from the spontaneous evaporation of the embalming fluid. The people met this point by proving that such fluid had been abundantly experimented upon by exposure to a very low temperature during an interval of several months, and also by spontaneous evaporation with a view of testing that very question, and that the results had in every case been negative. Special importance was given these experiments because of the well-known separation of octahedral crystals during the spontaneous evaporation of a hydrochloric acid solution of the white oxide, it having also appeared that, in the manufacture of the embalming fluid, the arsenic was used as white arsenic.

A very strong point was finally raised for the defence by the inability of the people's expert to state positively whether or not an embalming fluid of the above composition would diffuse as a whole through dead tissue, or its several parts would be imbibed at different rates of speed, the zinc portion becoming arrested by albumenoid material and being therefore outstripped by the arsenic, or *vice versa*. Experimental evidence upon this topic is entirely wanting, for although an investigation touching upon this subject was instituted in this laboratory, the results are not in such shape as to permit of their use in so important a case as a trial involving life. The first trial resulted in a failure of the jury to agree, and the second in an acquittal of the prisoner.—*Journal of Analytical and Applied Chemistry*, xv., No. 6.

THE SYNTHETIC POWERS OF MICRO-ORGANISMS.

By O. LOEW, University of Tokio, Japan.

AMONG all living organisms the micro-organisms, micrococci as well as bacteria, bacilli, and spirilli, are especially remarkable for their intensity of chemical activity. Oxidations and decompositions, reductions, and synthetical processes are effected on an extensive scale.

If we consider the destructive and the synthetical operations we must arrive at the conclusion that the former are necessary for carrying on the latter. The former yield not only the forces necessary for the synthetical work, but also the suitable atomic groups. It is certainly a highly interesting question of physiological chemistry to study the relations of the two different directions and to elucidate which are the groups that serve for the synthetic work. We must first consider the chemical structure of the compounds that can serve as nutrients, we must investigate the causes that bring about the transformation of potential into actual energy, and we must recognise above all that the proteids of the living protoplasm are chemically distinct from those of the dead. We must acknowledge that when the labile character of the former changes by atomic migration into a stable one the death of the cells has come.

Nutritive and poisonous qualities are relative conceptions. Poisons may become nutrients for bacteria when highly diluted, as phenol or acetic ether, and nutrients may become unfit for nutrition if the concentration reaches certain limits. Small chemical changes may convert a nutrient substance into a poison and again the poison into an indifferent substance.

As albuminous matter contains carbon, hydrogen, nitrogen, sulphur, and oxygen, we have to consider principally the question, which substances are suitable sources for the carbon, which for the nitrogen, which for the sulphur. Our experiments lead to the following conclusions :—

1. As sources of carbon can be used in neutral or feebly alkaline solutions, alcohols, phenols, organic acids, ketones, aldehyds, carbohydrates, ethers and esters, many alkaloids.

2. As sources of nitrogen can serve: ammonium salts, nitriles, amido-acids, amines, ureas, guanidines, alkaloids, nitrates, and nitrites.

3. As sources of sulphur may serve: sulphates, sulphites, hyposulphites, sulpho-acids, mercaptans, sulphones.

It is remarked in a note that the nucleins, which contain phosphoric acid in their molecule, are here left out of consideration.

The following conclusions are drawn for most of the non-pathogenic microbia :—

1. Hydroxylated acids are better than the corresponding non-hydroxylated ores, *e.g.*, lactic acid is better than propionic acid.

2. Polyvalent alcohols are more favourable for the development than the corresponding monovalent alcohols, *e.g.*, glycerin is better than propylic alcohol.

3. The nutritive quality of the fatty acids and monovalent alcohols decreases with the increase of the number of carbon atoms in their molecules. Thus acetic acid is better than butyric acid.

4. The entrance of aldehyd or ketone groups increases the nutritive properties; glucose is better than mannite.

5. I have observed neither nutritious nor poisonous properties in picro-nitric acid, chloral hydrate, pinakon, ethylendiamine, glyoxal, amido-acetal. Aceto-oxime, diacetonamin, and maleinic acid are very poor nutrients. According to B. Meyer, mesaconic, citraconic, paramethyl-succinic, dimethyl-succinic, and benzoyl-succinic acids are not capable of serving as food.

6. The poisonous properties are determined by the energy with which the unstable atoms of the living protoplasm are attacked.—*Central-Blatt f. Bacteriologie.*

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1894.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, February 10th, 1894.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 170 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from January 1st to January 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 170 samples examined all were found to be clear, bright, and well filtered.

Nineteen samples of water could not be taken owing to the very severe frost at the commencement of the month.

Deficient rainfall, so marked a feature of the year 1893, has also characterised the month of January of the present year. The actual rain at Oxford during the month just passed has been 1·74 inch, whereas the mean for 25 years is 2·26, showing a deficiency of 0·52 inch. The deficiency in the corresponding month of last year was 0·38 inch.

As regards the general quality of the Thames-derived waters, deduced from the results of analysis, they are almost identical, even to the third place of decimals, with the waters of January, 1893. As compared with the waters of October, November, and December, 1893, there is a minute increase in the organic carbon, and in the oxygen required for the combustion of the organic matter. In no case, however, does the increase affect more than the second decimal place, so that it is entirely unimportant. The usual seasonal variations in the quality of the waters have been as yet little marked, but with the not improbable advent of wetter and colder weather a continuance of these high conditions of purity—conditions which more resemble those of summer than of winter—must not be reckoned upon.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

SECOND PAPER: THE ANALYSIS OF BARIC CHLORIDE.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 82.)

Silver.—A number of different preparations of this metal, which served as one of the fundamental standards of reference, were used during the course of the work. For the final experiments pure argentic chloride remaining from earlier work was reduced by means of pure sodic hydrate and invert sugar, the invert sugar having been prepared in the first place by heating a strong solution of the purest obtainable cane-sugar with a little hydrochloric acid at 100°. After a very thorough washing the metal resulting from this reduction was fused upon hard-wood charcoal in the flame of an ordinary blast-lamp, and divided into two parts.

One half of this silver was purified at once by electrolysis according to the manner described in a former paper (*Proc. Amer. Acad. Arts Sci.*, xxviii., 22), and was used in Analyses 30, 31, 32, 35, 36, and 37. The other half was dissolved in the purest nitric acid, and precipitated again with hydrochloric acid; then the argentic chloride was digested with aqua regia, very thoroughly washed with water, and again reduced to the metal. The last product was fused into large buttons upon sugar charcoal, and purified by electrolysis as before. The current obtained from seven or eight gravity cells is amply sufficient for the purpose. This doubly refined silver was used in Experiments 33, 34, 38, 39, 40, 41, and 43.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences.*

The silver used in Experiment 42 was prepared in the first place by Mr. H. F. Brown, according to the cuprous ammonic sulphite method of Stas ("Untersuchungen, &c." (Aronstein), pp. 34 and 113). Although the substance thus prepared gave every outward evidence of perfect purity, it was once again purified, this time by means of the electrolytic method used in the case of the previous specimens.

The three samples of beautiful crystals of silver thus obtained by electrolysis naturally contained a minute amount of imprisoned mother-liquor, which is best expelled by fusion. Many precautions were taken to prevent the absorption of an impurity during this process.

In the first trials pure hard-wood charcoal was used to support the metal during its fusion in the flame of the ordinary blast-lamp (Experiments 30, 31, and 32). Afterwards a cupel of sugar charcoal was substituted for the wood charcoal. Such cupels are readily made by mixing finely-powdered pure sugar charcoal with about a third of its weight of pure powdered sugar, and igniting in closed moulds. The silver used in Analyses 35, 36, 38, 42, and 43 was fused in this way.

A possible absorption of sulphur from illuminating gas being feared, a number of buttons of silver were fused upon the sugar charcoal cupels by the use of a blast-lamp in which only pure alcohol, vapourised in a steam-bath, was burnt. Such silver was used in Experiments 33, 34, 37, 39, and 40. All of these specimens of silver had been cooled with care in the centre of a strongly reducing flame, to prevent the absorption of oxygen; and any button which showed a trace of such absorption was of course discarded. Proof has already been given (*Proc. Amer. Acad. Arts Sci.*, xxv., 198) that no oxygen is held after such treatment; but in order to "make assurance doubly sure," 3½ grms. of the purest crystals were placed upon a boat made of sugar charcoal, enclosed in a stout porcelain tube, and fused in a vacuum (Experiment 41).

The results obtained from these different varieties of silver may well be recorded here, although the details must be reserved until nearly the end of the present paper. The first specimen of silver fused upon wood charcoal was used in experiments which were vitiated by other serious errors, so that the results from it need not be given. The figures given below represent the amount of silver required exactly to precipitate 100,000 parts of baric chloride.*

1.	1st specimen,	sugar charcoal,	illuminating gas	103·600
2.	„	„	alcohol	103·604
3.	2nd	„	illuminating gas	103·600
4.	„	„	alcohol	103·599
5.	„	„	fused in vacuum	103·599
6.	3rd	„	illuminating gas	103·600
		Average..		103·600

Of these figures 2, 5, and 6 represent single results, and the other figures represent averages. Since a number of samples of baric chloride and a number of different methods of comparison were used in the individual cases, the averages, which to some extent eliminate the differences, are more reliable than the single results. It is evident that the different varieties of silver were quite as nearly alike as the accuracy of our present processes demands.

The investigation of the silver closed with a direct determination of the amount of sulphur present in a sample which was purposely made under conditions as favourable as possible for the retention of this impurity. Twelve grms. of silver, which had been prepared by the sulphite method and fused three times successively for a long period in the flame of an ordinary blast-lamp were dissolved and precipitated by electrolysis in a solution of silver nitrate prepared from the same silver. The residual electrolyte, which must have contained all the sulphur, was much diluted, freed from silver by the addition of hydrochloric acid, and evaporated on the steam-bath to free it from nitric acid. This solution yielded 1·4 m.grms. of baric sulphate, corresponding to 0·2 m.grm. of sulphur. Hence under these conditions the silver held only $\frac{1}{70000}$ of its weight of sulphur; and it is fair to conclude that according to the usual method of subjecting the silver only to a single brief fusion not more than $\frac{1}{300000}$ of its weight would be absorbed. This result is in entire accordance with the quantitative and qualitative results already described; it shows that silver fused once in an illuminating gas may be used without appreciable error for all ordinary work.

The preparation of pure water, alcohol, sulphuric and nitric acids, and all other necessary materials, has been discussed in previous papers (*Proc. Amer. Acad. Arts Sci.*, xxvi., 245—249; xxviii., 23).

Standard Solutions.—Several standard solutions were so constantly used during the research that they may well be described at the beginning. In the first place, exactly a grm. of silver was dissolved in a slight excess of nitric acid, with the usual precautions (*Ibid.*, xxv., 198; xxviii., 24), and diluted exactly to a litre. A solution of pure hydrochloric acid was then made of equivalent strength by comparison with pure sodic carbonate, and verified by comparison with the silver solution. This last comparison is not easily made, for the argentic chloride separates but slowly from a solution so dilute. It was found most convenient to add a very slight excess of silver, to warm, agitate, and filter the solution, and to determinine the excess in the filtrate by means of an equivalent solution of ammonic sulphocyanate, after the method of Volhard. Sanger (*Proc. Amer. Acad. Arts Sci.*, xxvi., 34) has pointed out that the solubility of argentic chloride seriously affects the accuracy of this method unless the argentic chloride is filtered off before the addition of the sulphocyanate; and the experience of this Laboratory had independently led to the same conclusion. It is to be hoped that Clemens Winkler observed this precaution in his interesting analyses of cobaltous and nickelous chloride (*Zeit. Anorg. Chem.*, iv., 10); if not, the atomic weights obtained are probably too high.

The three equivalent solutions of argentic nitrate, hydrochloric acid, and ammonic sulphocyanate each corresponded exactly to a m.grm. of silver for each c.c. These solutions are referred to whenever a standard solution is mentioned below.

It is needless to say that the measuring apparatus was all calibrated with great care; moreover, for the final experiments the solutions were weighed in small flasks provided with tightly-fitting graduated pipettes as well as measured. This last precaution was hardly necessary, however. Of course, the ordinary methods of volumetric analysis are not applicable to the determination of atomic weights; but when the greater part of a reagent has been weighed out the last few m.grms. may be added by the measurement of a very dilute solution with an accuracy quite equal to that obtainable upon a balance.*

(To be continued.)

The Sanitary Institute.—The Council of the Institute have accepted an invitation received from the Lord Mayor and Citizens of Liverpool to hold their next Congress and Exhibition in that city in the Autumn of this year.

Bacteriology.—Dr. A. B. Griffiths will commence on March 1 a course of lectures on Bacteriology, with special reference to the chemistry of the subject. The lectures and laboratory work will be given at the Central School of Chemistry and Pharmacy, Marylebone Road, N.W.

* The results obtained from Stas's second method, described later, are omitted from this series.

* This point, among others, seems to have been misunderstood by G. Hinrichs, of the College of Pharmacy, St. Louis. (CHEM. NEWS, lxviii., 171).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Annual General Meeting, February 9th, 1894.

Prof. A. W. RÜCKER, M.A., F.R.S., President, in the Chair.

THE Annual Report of the Council was read by the PRESIDENT.

Dr. ATKINSON read the Treasurer's Report and also an obituary notice of the late Prof. Tyndall.

The adoption of the reports was moved by the PRESIDENT and carried *nem. con.*

Dr. Chichester Bell and Mr. Griffiths were appointed Scrutators, and subsequently declared the following gentlemen duly elected to form the new Council:—

President—Prof. A. W. Rücker, M.A., F.R.S.

Vice-Presidents—Walter Baily, M.A.; Maj.-Gen. E. R. Festing, R.E., F.R.S.; Prof. J. Perry, D.Sc., F.R.S.; Prof. S. P. Thompson, D.Sc., F.R.S.

Secretaries—H. M. Elder, M.A., 50, City Road, E.C., and T. H. Blakesley, M.A., M.Inst.C.E., 3, Eliot Hill, Lewisham, S.E.

Treasurer — Dr. E. Atkinson, Portesbery Hill, Camberley, Surrey.

Demonstrator — C. Vernon Boys, F.R.S., Physical Laboratory, South Kensington.

Other Members of Council — Shelford Bidwell, M.A., LL.B., F.R.S.; W. E. Sumpner, D.Sc.; Prof. G. Fuller; J. Swinburne; G. Johnstone Stoney, M.A., F.R.S.; R. E. Baynes, M.A.; Prof. G. M. Minchin, M.A.; L. Fletcher, M.A., F.R.S.; Prof. O. Henrici, Ph.D., F.R.S.; Prof. S. Young, D.Sc., F.R.S.

Prof. REINOLD proposed a hearty vote of thanks to the Lords of Committee of Council on Education for the use of the rooms and apparatus in the Royal College of Science. This was seconded by Prof. J. V. JONES and carried unanimously.

Votes of thanks were similarly accorded to the Auditors, Mr. A. P. Trotter and Mr. R. Inwards, on the motion of Mr. WATSON, seconded by Prof. FULLER; and to the Officers of the Society, on the motion of Dr. BURTON, seconded by Mr. TROTTER.

At an ordinary Science meeting then held, Mr. OWEN GLYNNE JONES, B.Sc., read a paper on the "*Viscosity of Liquids*," and exhibited the apparatus used in his experiments.

The method employed consists in measuring the speed at which a small sphere travels through the liquid under the action of gravity. As Prof. Stokes had shown, the velocity of a sphere falling in an infinite liquid becomes constant, this velocity being given by the equation—

$$V = \frac{2}{9} g a^2 \frac{b-\rho}{\mu},$$

where a is the radius of the sphere, b its density, ρ the density of the liquid, and μ its viscosity. If sliding friction exists between the sphere and liquid the equation becomes—

$$V = \frac{2}{9} g a^2 \frac{b-\rho}{\mu} \frac{\beta a + 3\mu}{\beta a + 2\mu},$$

where β is the coefficient of friction.

In making the experiments small spheres (usually of mercury) were allowed to fall through a burette containing the liquid, and the time taken to travel the distance between two marks about 50 c.m. apart noted. The radii of the spheres being small it was considered better to deduce this from the mass. Direct determination of such small masses being difficult, a larger mass (M) was taken, weighed, and divided into, say, ten or twelve parts, and the speed of falling of each part observed in a liquid of constant viscosity. The velocity V, with which a sphere containing the whole mass would have fallen, was deduced from the equation—

$$V^{\frac{1}{3}} = \Sigma v^{\frac{1}{3}}.$$

Similarly, the mass of any part which falls with a velocity v is given by—

$$m = \left(\frac{v}{V}\right)^{\frac{1}{3}} . M.$$

In this way the author had been able to determine the mass of a sphere weighing only about 0·003 grm. to four significant figures.

Referring to experiments made with a view to ascertaining whether sliding friction existed, the author said the divergence from the simpler formula did not exceed experimental errors.

In determining viscosity, changes of temperature were found to be of great importance, especially in the case of glycerin, whose viscosity varies as much as 10 per cent for 1° C. Small differences of temperature between different parts of the liquid are, however, not very serious, provided the mean temperature be known, for the mean speed observed is shown to be that corresponding to the mean temperature. To determine viscosity accurately at a given temperature, very delicate thermometers must be employed. Most of the liquids experimented on were bad conductors of heat, and hence required considerable time for the temperature to become uniform. Differences in temperature could readily be detected by observing if the speed of descent of a small sphere varied at different parts of its path. The author suggested that this fact might be used to determine the thermal conductivity of liquids heated at the top by Forbes's method. The falling sphere would form a thermometer of almost infinitesimal thermal capacity. For most oils spheres of water coloured with eosin could be employed to determine the viscosity. A water drop of 1 m.m. radius was found to fall 1 inch per hour in castor oil at 8° C.

To determine the variation of viscosity with temperature a special apparatus was used with which observations could be made in rapid succession by simply inverting the tube containing the liquid and the falling sphere. In Mr. Troughton's viscosity experiments, which were somewhat analogous to those described, surface tension complicated the results considerably; the author's aim had been to eliminate such disturbing influences.

Professor EVERETT in a written communication suggested that the motion of the liquid sphere be checked by using beads of quartz or glass.

Lord RAYLEIGH pointed out in a letter that the formula employed related to a solid sphere, and thought it not legitimate to use it for liquid spheres, for the tangential forces at the surface would set the interior liquid in relative motion, and modify the resistance experienced. He also thought the existence of a finite coefficient of sliding friction between two fluids an impossibility.

Mr. WATSON said temperatures might be kept constant for days together by Ramsay and Young's vapour jacket.

Dr. SUMPNER thought the surface tension of such small spheres of mercury was so very large that they would act practically like solids. The want of solidity might be of importance when the two liquids were very nearly alike in density and other properties.

Mr. BLAKESLEY said that at high velocities the falling sphere might get a palpitating motion in addition to the gradual descent, and this might introduce errors.

Prof. PERRY considered that the experiments on the velocity of a small sphere, and those of the two parts in which it was divided, which showed that—

$$V^{\frac{2}{3}} = v_1^{\frac{2}{3}} + v_2^{\frac{2}{3}},$$

proved the simple formula used to be correct.

Mr. BOYS enquired if any tests had been made on the constancy of dimensions of the spheres used. He would expect that in the case of water and oil, for example, that

mutual contamination would take place. Speaking of the indirect method of determining the masses of small spheres, he thought direct weighings might be made, for, as the President and Prof. Poynting had shown, the balance might be immensely improved.

Prof. S. P. Thompson suggested that small globules of aluminium or slag might be used.

Dr. C. V. Burton thought Lord Rayleigh's criticism important, and that large corrections might be necessary. He failed to see how the large surface tension mentioned by Dr. Sumpner could prevent internal circulation.

Mr. Trotter said Lord Rayleigh's point might be tested by using a sphere of oiled wax.

Mr. Boys mentioned that Lord Rayleigh had shown in the case of soap rings that variation of surface tension, due to stretching or compression, produced stability. The same phenomena would probably retard internal circulation.

The President said there was little doubt that internal circulation as mentioned by Lord Rayleigh would modify the velocity.

In his reply Mr. Jones said he could not imagine how, in pure liquids, internal motion in the falling spheres could be set up. In answer to Mr. Boys he had found slight changes in the masses of the water spheres after being used many times, but this was a question of days. During an ordinary series of observations the dissipation was too small to be observed.

After the meeting had been adjourned Mr. Boys and Dr. Burton considered the question of internal circulation, and the latter pointed out that with perfectly liquid spheres there would be infinite slip, and the coefficient of sliding friction β would be zero. The velocity of descent would therefore be $\frac{2}{3}$ times that given by the first equation.

NOTICES OF BOOKS.

Johnston's Elements of Agricultural Chemistry. From the Edition of Sir Charles A. Cameron, M.D. Revised, and in great part Re-written, by C. M. Aikman, B.Sc., F.R.S.E., &c. Seventeenth Edition. Edinburgh and London: W. Blackwood and Sons. 1894.

For all the seventeen editions which it has passed through, this must be considered to a great extent as a new work. The tenth edition, which appeared in 1877, was dedicated to Sir J. B. Lawes, F.R.S. The twelfth edition, got up by Sir C. A. Cameron in 1881, was inscribed to Dr. Jas. Dewar, F.R.S., and the present issue is dedicated to Dr. Bernard Dyer.

Many of the new additions and alterations have decidedly increased the value of the work.

In the second chapter we regret to see an error in the table of the atomic weights of the elements. Platinum is still given as higher than gold, the former being made = 197, and the latter = 196·8.

In remarking that caustic potash "has a somewhat nauseous odour," the author contradicts an error which has found its way into many text-books.

The remark that of the 5000 species of flowering plants of central Europe only 300 grow on peaty or boggy soils is very significant.

A much more generally appreciable observation is that found in the chapter on the origin and classification of rocks. "How little have either tenants or proprietors hitherto been guided by 'scientific insight' in their choice of the localities in which they desire to live."

The chapter on the relations between plants and the soils in which they grow, and the manures applied to them, is exceedingly instructive. Due mention is made of the abundance of water-cress—Mr. Aikman might have added "and of forget-me-not"—at the margins of streams rich in calcium carbonate. Attention is called to the changes which naturally, in the course of ages, come over soils, and are manifested by corresponding changes in the character of the vegetation. The question is raised whether such changes are due to the exhaustion of some important principle in the soil, or to the presence of noxious matters in the subsoil?

These considerations naturally lead to the improvement of soils by drainage, tillage, and mixing. The *rationale* of these operations is laid down in a most judicious manner.

The influence of trees on the rainfall is scarcely brought out sufficiently. If they do not increase the total amount of atmospheric precipitation, they distribute it. Where deforestation has been general, the weather consists of irregular alternations of drought and flood. Perhaps of all the ruinous agencies to which land can be exposed, the most to be deprecated is the action of goats.

The use and abuse of lime are next discussed. Unlike certain authorities, *e.g.*, M. Ville, he does not consider that a supply of calcareous matter is universally needed.

The chapter on irrigation is concluded with the following truthful remark: "Irrigation, however, is only suited for warm climates. In cold damp climates, with heavy clayey soils, its effects are far from favourable" (p. 224). We are therefore surprised to find (p. 336) the author, speaking on the utilisation of sewage, giving his opinion to the effect that "where land of a suitable quality can be got and its situation is favourable, the sewage should be directly applied to it without any previous chemical treatment." Now, what has been previously said concerning irrigation with river water must apply *a fortiori* to sewage irrigation, which, for sanitary reasons, must be allowed to flow upon the land, quite irrespective of the weather. It seems that Mr. Aikman speaks of the chemical treatment of sewage in the past tense. He surely must be aware that the A B C process is still in regular and successful operation, and that the manure produced finds a regular and increasing sale at a price certainly not less than that of the precipitants. Other chemical processes are also in constant use and are found to give satisfaction.

With the sole exception of the passages on the sewage question, the work before us must be most warmly recommended to all persons interested in agriculture.

A Manual of Practical Assaying. By H. Van F. Furman, E.M. First Edition. New York: John Wiley and Sons. 1893.

It would be no small boon if some competent authority could fix the acceptation of the term assaying and its paronyms. Some writers at present make it a mere synonym for analysis, others confine it to operations, however conducted, the object of which is technical or commercial. Others, again, restrict it to so-called fire-methods, such as the Cornish copper assay. The author seems to take this last view, though he says that assaying includes all those operations of analytical chemistry which have for their object the determination of the value of ores and metallurgical products. He includes, however, the analysis of water, acidimetry, and alkalimetry, chlorimetry, &c.

Mr. Furman's remarks on sampling are very exhaustive and trustworthy.

In the list of blowpipe tests, as here given, we find a very useful feature—mention of "interfering elements," substances which if present may lead the experimentalist astray.

We are sorry to observe the prominence given to the Baumé hydrometer, though either the Twaddle instrument or the direct specific gravity hydrometer must be admitted to be preferable.

The tables here given are very useful as showing the difference between the British Imperial gallon = 70,000

grain measures of water and the American gallon of 58,318 grain measures, which are sometimes confounded.

We notice in the table comparing the Baumé scale with direct specific gravity, 46° B. is made = 1·44638. In other standard manuals its value varies from 1·434 to 1·468!

The atomic weight of gold is here given as 196·2, whilst that of platinum is made = 197·0.

A most valuable compilation is the table of the properties of precipitates, showing the manner in which they are obtained, their composition, conditions of solution, solubility, contaminants, method of preparation for weighing, and state in which they may be weighed.

Instructions are duly given for the electrolytic determination of copper, iron, nickel, and cobalt, and for an electrolytic separation of iron and alumina.

No notice seems to have been taken of the spectroscopic methods for the recognition of metals which are sometimes of great technical importance.

Metallurgists and mining engineers will find this work a useful addition to their libraries.

The Indian Journal of Pharmacy: a Monthly Record of the Chemical, Drug, and Allied Trades throughout India, Burmah, China, and Japan. Edited by Roger S. Chew, M.D. Vol. I., No. 1. Calcutta, January 6, 1894.

It is certain that in India and the adjoining countries there must exist no small number of vegetable products which have never yet been systematically examined, whether from a purely scientific point of view or from that of their pharmaceutical and technical applications. Hence our new contemporary has our best wishes.

It appears that a multitude of substances rich in odoriferous principles are overlooked and even thrown to waste. We read that "year by year tons of rich material go waste in Calcutta in the shape of oranges, lemons, pumloes, champa, jessamine, and other oil-yielding flowers and fruits, that would return a very profitable revenue to anyone collecting them for the purpose of extracting the oil which at present has to be imported at great cost from various parts of the world."

It appears that Symes and Co., of Simla, have succeeded in eliminating, on a commercial scale, the emetic property from ipecacuanha. The value of the drug in the treatment of dysentery is thus greatly enhanced.

A less satisfactory fact is that "electro-homœopathy," the "suggestive" treatment of disease, &c., have been introduced into India, and are becoming rampant.

Agricultural Journal. Published by the Department of Agriculture of the Cape Colony. VI., No. 26.

Complaints are made, with justice, of the careless sampling of manures, which occasions much annoyance and discredit both to manufacturers and analysts.

Attention is called to the cultivation of silk. There is no country in the world where the mulberry tree flourishes better than in South Africa. The worms keep healthy and the quality of the silk is good.

Ants are very troublesome in the orchards and vineyards. Carbon bisulphide poured down into the centre of the nest seems to be the most effectual agent for their suppression.

The irrigation-conduits are damaged by a species of fresh water-crabs, known as "yabbies," which perforate the sides and cause the water to run to waste. The introduction of eels seems to be the best remedy.

Practical Inorganic Chemistry. Tables and Notes adapted for the Science and Art Department Syllabus, 1893. By W. French, B.A., F.I.C., F.C.S. Bury: E. W. Smith.

This is one of those meagre elementary books for which it is scarcely possible to suggest a *raison d'être*. Surely anyone who wished to study the reactions of the few metals here selected might have found elsewhere all the information necessary.

CORRESPONDENCE.

EXAMINATIONS.

To the Editor of the Chemical News.

Sir,—Early in this century it was asserted, as a postulate, that all teachers are thieves, and in accordance with this tenet our present system of examinations was elaborated in order that a thief might be set to catch a thief. This I have before pointed out in your columns. Now that so great a teaching light as Professor Ramsay has given expression to the same idea, there is some hope that the time is at hand when the teacher will no longer be set in a class by himself among professional men.—I am, &c.,

One of the Thieves,
alias A. G. Bloxam.

Goldsmiths' Institute, New Cross, S.E.
February 20, 1894.

EXAMINATIONS.

To the Editor of the Chemical News.

Sir,—Your correspondents, Dr. Tilden, Mr. Groves, Prof. Ramsay, and Mr. Thomson, seem agreed that the system of examinations in higher education is not the Heaven-sent method of distinguishing between the competent and the worthless student which some people imagine.

It appears from Mr. Ramsay's important letter that the examinational system was devised not in the interests of Science, but was a "protest against favouritism." If he is correct, which I see no reason to doubt, it appears that to remove a small possible evil a greater one has been committed. Favouritism is not desirable, but it is a very small matter as compared with the scientific progress and eminence of the country.

Mr. Ramsay puts his finger on the reason why incompetent men "pass" when he writes "they have from their youth upwards been trained in examinational methods." They have been taught by their coaches the secret which the first Napoleon employed in his tactics—that of being strongest at the point of contact.

I am not aware that any person or any body of men "advocate leniency in examinations," though there are not a few who think that in scientific subjects examination is altogether a delusion.

The only person who can judge of the competence of a student are the teachers who have watched him regularly in the laboratory—chemical, physical, or biological—and whose "*testamur*" is far preferable to any number of marks.—I am, &c.,

J. W. Slater.

BLEACHING LINEN.

To the Editor of the Chemical News.

Sir,—I have read with some surprise the article by G. Geisenheimer (Chemical News, vol. lxix., p. 69) on "An Application of Sodium Silicate" for bleaching linen, as the difficulty and uncertainty he speaks of in bleaching linen *a pure snow white* are unknown in this country. I take it, assuming by the name, that he is speaking of bleaching as it is at present done in Germany. His article evidently cannot refer to bleaching linen on an extensive system, as it is conducted in the North of Ireland, but I presume has reference more to the system where

washing, &c., is carried on for domestic purposes, where family linens are sent to the laundry to be washed and bleached. If he means bleaching linen received direct from the looms of the manufacturer, the German system, as described by him, must be at least two generations behind the times.

Considering the chemical knowledge possessed by the Germans, I am surprised to find that in its application to linen bleaching they have not kept to the front, but have lagged so very far behind, if I have gauged correctly the tenor of G. Geisenheimer's article.—I am, &c.,

STEPHEN M'DOWELL.

12, Queen Street, Belfast,
Feb. 19, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 6, February 5, 1894.

The Death of M. Fremy. — The obsequies of this eminent *savant* took place in the morning of February 5 in presence of a great crowd of colleagues, pupils, and friends. According to the expressed desire of the deceased no orations were delivered at the grave. M. Friedel is now the *doyen* of the Chemical Society.

Campholene.— M. Guerbet.— Campholene has been prepared for the first time by Delalande by causing phosphoric anhydride to react upon campholic acid. It is preferable to prepare this carbide by distilling campholyle chloride in presence of a trace of phosphoric anhydride, $C_{10}H_{17}ClO = HCl + CO + C_9H_{16}$. The yield is 73 per cent. It is colourless, its odour is like that of turpentine, and its taste is burning. It boils at 134° under a pressure of 758 m.m. Its vapour density is 4·26, theory demanding 4·28. The specific gravity of the liquid is 0·8115 at 0°. It has no rotatory power.

The Thermic Value of the Functions of Orcine.— M. de Forcrand.—The author assigns 39·68 cal. as the mean value of the two functions.

Attenuation of the Venom of the Viper by Heat. Inoculation of Guinea-pigs against this Venom.—C. Phisalix and G. Bertrand.—Classic authors admit that the venom of the viper may be submitted to ebullition without losing anything of its poisonous properties. The similarity of the active principles of this venom to the diastasic substances renders this assertion *a priori* improbable, and a systematic study of the action of heat has led us to contrary conclusions. We have further recognised that this venom after exposure to heat possesses vaccinating properties.* The failures of earlier experimentalists may have been due to the circumstance that they used too large quantities of the heated venom, so that in spite of a partial destruction there still remained enough toxic matter to prove fatal. Hence we have operated with a limited quantity, the effects of which we had ascertained by earlier experiments. The minimum fatal dose for a guinea-pig weighing ½ kilo. corresponded to 3·10ths m.grm. of the dry poison. This dose, dissolved in 1·5 c.c. of salt water, was introduced into a narrow glass tube which was sealed at the lamp. The tube was then placed in a large volume of water of the desired temperature, taken out after a fixed time, and a guinea-pig was inoculated with the contents. We have thus found that at 60°—70° the attenuation of the venom is already very considerable. After heating for fifteen minutes it proved fatal only after the lapse of thirty-six to forty-eight hours, whilst the same dose of the venom in its original condition proved fatal in ten hours. Above 75° the action of the temperature became very manifest. The animal presented some slight symptoms of echidnism, but it survived the inoculation. The symptoms are the slighter the longer the heating is prolonged and the higher the temperature. In general they were null after the venom had been kept for five minutes at 80°, or for fifteen minutes at 75°. Still, by a short application of a high temperature we have obtained an unexpected result. On heating the venom to ebullition for twenty or twenty-five seconds, we have dissociated the local from the general effects of poisoning. The former were suppressed, but the latter remained, and occasioned death in twenty-four or forty-eight hours. Such a distinct association led us to conceive more important modifications, and to enquire if the heated venom might not become a "vaccine" for the original venom. We therefore submitted to the test of mortal inoculation guinea-pigs which had received some days previously an injection of venom attenuated by heat, and we observed that the animals not only did not perish, but that they did not present any appreciable symptom of poisoning. We repeated these experiments several times with the same success upon guinea-pigs which had received previously injections of venom heated for five minutes to 75°, 80°, and 90°. The experiments showed that the venom which had been heated raises the temperature of the subject. The original venom, on the contrary, even in doses of 1·10th m.grm. always reduces the temperature. This hyperthermia is still more marked at 80° and 90°. Further, the heated venom has a vaccinic action, whilst the original venom, even in minute doses, produces merely a slow and progressive toleration of the poison, but no real vaccination. We believe ourselves, therefore, authorised to formulate the following conclusions:—In the toxic constituents of the venom there is reason to distinguish (1) a substance with a phlogogenous action comparable to certain diastases, for which we propose to reserve the name *echidnase*; (2) a substance having a general action powerfully affecting the nervous system, disturbing the functions of the vasomotor apparatus, and sufficient to bring on death. Its effects are shown in the guinea-pig by a considerable hypothermia. We call this substance *echidnotoxine*.

* The term vaccinating and its paronyms are used here, not to signify a preventive to variola, but in a generalised sense.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. viii., No. 94.

Report Submitted by M. Imbi on behalf of the Committee for Mechanical Arts on the Memoir by J. Schlœsing, jun., on the Hygroscopic Properties of Textile Fibres.—The author gives the results of his numerous experiments on cotton, silk, and wool in the shape of tables and also of curves.

Revue Universelle des Mines et de la Metallurgie. Series 3, Vol. xxiv., No. 3.

The Assay of Manganese Oxides by means of Oxygenated Water.—A. Carnot.—From the *Bull. de la Soc. Chimique.*

The Precipitation of Manganese by Hydrogen Peroxide and Ammonia.—A. Carnot.—From the *Bull. de la Soc. Chimique.*

Separation and the Volumetric Determination of Lean.—Lindemann and Motteu.—From the *Bull. de la Soc. Chimique.*

Proportion of Fluorine in Teeth.—Dr. E. Wrampelmeyer.— This paper requires the accompanying plate (III). The author's method is based upon that of Carnot (*Comptes Rendus*, cxiv., 750 and 1003, and cxv., 243). The author remarks that the soundness of teeth cannot be decided from their proportion of fluorine.—*Zeitschrift fur Analytische Chemie*, xxxii., Part 5.

MISCELLANEOUS.

Society of Public Analysts.—Sir Charles Cameron has been re-elected to the Presidency of the Society of Public Analysts.

Camera Club Photographic Conference, 1894.—The 1894 Conference will be held in the theatre of the Society of Arts on Monday and Tuesday, April 23 and 24, under the presidency of Capt. W. de W. Abney, C.B., R.E., D.C.L., F.R.S., P.R.A.S. On Monday, April 23, at 3 p.m., the President will open the Conference at the Society of Arts, and papers will be read from 3 to 6 p.m. At 8 p.m. the Conference will be continued, and papers will be read from 8 to 10 p.m. On Tuesday, April 24, at 3 p.m., the Conference will be renewed at the Society of Arts, and papers will be read from 3 to 6 p.m. In the evening a lantern-slide exhibition will be given in the theatre of the Society of Arts, for which special tickets will be required. On Wednesday, April 25, at 7.30 p.m., the Annual Dinner for members and friends will be held. The Members' Annual Exhibition of Photographs will be commenced at the Club on the first day of the Conference.

The Chemical Laboratory of Wiesbaden.—The Chemical Laboratory of Geh. Hofrath Prof. Dr. Fresenius at Wiesbaden enjoys a very large attendance. In the winter term, 1893—1894, there were 65 students on the books. Of these, 35 were from Germany, 10 from England, 6 from Sweden and Norway, 5 from North America, 3 from Belgium, 2 from Austria, 2 from Russia, 1 from Holland, 1 from Italy, and 1 from Batavia. Besides the Director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged as teachers in the establishment Prof. Dr. H. Fresenius, Prof. Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, Dr. W. Lenz, and architect F. Brahm. The assistants in the Instruction Laboratory were 3 in number, in the Private Laboratory 18, and in the Versuchsstation 2. The next summer term begins on April 24. During the last term, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory and the Versuchsstation on behalf of manufacture, trade, mining, agriculture, and hygiene.

MEETINGS FOR THE WEEK.

MONDAY, 26th.—Society of Arts, 8. (Cantor Lectures). "The Decorative Treatment of Artificial Foliage," by Hugh Stannus, F.R.I.B.A.
TUESDAY, 27th.—Royal Institution, 3. "Locomotion and Fixation in Plants and Animals," by Prof. Charles Stewart, Pres.L.S.
—— Medical and Chirurgical, 8.30.
—— Institute of Civil Engineers. 8.
—— Photographic, 8.
—— Society of Arts, 8. "Goldsmith's Work—Past and Present," by Mrs. Philip Newman.
WEDNESDAY, 28th.—Society of Arts, 8. "Rainfall Records in the British Isles," by G. J. Symons, F.R.S.
—— British Astronomical, 5.
THURSDAY, March 1st.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "The Vendânta Philosophy," by Prof. Max Müller, M.A.
—— Chemical, 8. "Aërial Oxidation of Terpenes and Essential Oils," by C. T. Kingzett.
FRIDAY, 2nd.—Royal Institution, 9. "The Theory of the Cochlea and Inner Ear," by Prof. J. G. McKendrick, M.D., F.R.S.
—— Geologists' Association, 8.
—— Quekett Club, 8.
SATURDAY, 3rd.—Royal Institution, 3. "Light, with special reference to the Optical Discoveries of Newton," by the Right Hon. Lord Rayleigh, F.R.S.

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The Vendor Company's process is that worked under the Patents particularised in the Contract of Sale. To enable intending subscribers to appreciate the merits of the process, its advantages over other processes for the same purpose, and the highly remunerative results likely to accrue from its operations, they are invited to peruse the accompanying Reports, made to the Vendor Company by the distinguished scientist, Professor John Hopkinson, F.R.S., late President of the Institution of Electrical Engineers, Mr. James Swinburne, Member of Council of the Institution of Electrical Engineers, and others.

It will be observed that Mr. John Leith, of St. Helens, the well-known Lancashire Alkali Manufacturer and Chemical Engineer, in his Report states:—"I estimate that £100,000 will provide all necessary working capital, buildings, land, plant, and machinery, capable of turning out annually 6,400 tons (70 per cent) Caustic Soda and 13,320 tons (36 per cent) Bleaching Powder, and that the profit on the manufacture, in combination, of the above 19,720 tons of Caustic Soda and Bleaching Powder by this Electrolytic process should be about £110,000 per annum."

The required Capital will be provided by the present issue of 10 per cent Preference Shares, the Vendor Company accepting the purchase-money as to seven-tenths in Ordinary Shares, and the balance in Preference Shares or cash, at the option of the Directors.

In addition to erecting works for manufacture, it is proposed to grant licenses to Paper and Soap Makers, Oil Refiners, Bleachers, and other large users of these chemicals who desire to manufacture Caustic Liquor or Bleach for themselves; and it is anticipated that a considerable additional revenue will accrue from this source, as well as from the sale of, or licence to use, the Foreign Patents. The apparatus for the manufacture of Caustic Liquor and Bleach by the Electrolytic Process being very compact, simple, and inoffensive in working, can easily be erected on the user's premises at a small outlay, and worked by spare engine power, thus saving great expense in solidifying the Soda and absorbing the Chlorine in lime for transport, as well as all charges for packing in drums or casks, and carriage.

The Company acquires of the Vendor Company all the British Patents in respect of the different Inventions used for the process, and such Patent rights as have been obtained or applied for, in respect of some of the Inventions, in France, Austria, Belgium, Italy, Norway, the United States, and Canada, and all other rights of the Vendor Company in respect of the Inventions.

The Contract of Sale, dated 16th February, 1894, is made between the Electrolytic Caustic Soda and Chlorine Trust, Limited (in this Prospectus called the Vendor Company), and this Company, and provides for the purchase of all the British Patents and the Foreign and Colonial Patent rights above referred to, for £100,000, payable, as to £70,000, in fully-paid Ordinary Shares of this Company, and the remainder in cash or Preference Shares, at the option of the Directors, subject to the optional right of C. Townsend Hook & Co., Ltd., to a licence free of royalty to use the inventions at their own works in the business of paper manufacturers [this right was granted by the Patentees for services rendered to them, and the Vendor Company purchased with this reservation], and subject also to the optional rights of John Collins, Ltd., Messrs. Henry Bruce and Sons (Kinleith Paper Mills), The Hendon Paper Works Company, Ltd., Messrs. P. Dixon and Son, Messrs. John Riley and Sons, The Horton Kirby Paper Works, Edward Lloyd, Ltd. (*The Daily Chronicle* Paper Mills), The Glory Paper Mills Company, Ltd., The East Lancashire Paper Co., Ltd., The Ellangowan Paper Co., and Dixon, Horsburgh, and Co., Ltd., to manufacture Caustic Soda and Bleach, at a royalty of 15 shillings per ton for their own use, at their own works, to the extent, in the aggregate, of 561 tons per week, which at 50 working weeks in the year, would amount to 28,050 tons per annum.*

The Vendor Company is the promoter of this Company, and has fixed the amount of the purchase-money. It pays all the costs and charges of the formation of this Company up to and including allotment. The Contract of Sale is the only contract to which this Company is a party, but as the above-mentioned conditional agreements for licences and other business contracts of the Vendor Company may technically be deemed contracts within the meaning of Section 38 of the Companies' Act, 1867, applicants for Shares shall be deemed to waive the insertion of the dates and names of the parties to any other Contract.

A search was made in the Patent Office on behalf of the Vendor Company, by Messrs. Newton and Son, the well-known Patent Agents, for any British Patents likely to constitute anticipations of the inventions relating to the process, and they submitted the results of the search to Mr. J. Fletcher Moulton, Q.C., F.R.S., whose favourable opinions may be seen by any intending subscriber.

Samples of Caustic Soda and Bleaching Powder, manufactured by the Vendor Company at Snodland, also the originals of the above-mentioned reports, all of which are addressed to the Vendor Company, can be seen at the offices of the Company. The opinions of Mr. Moulton, the Contract of Sale, and the Memorandum and Articles of Association, can be seen at the Offices of the Solicitors to the Company.

Applications for Shares should be made on the enclosed form; accompanied by the payment of 10 shillings per Share, and should be sent to the Bankers, or to the Secretary at the Offices of the Company. Prospectuses and Forms of Application can be obtained of the Bankers, Brokers, and the Secretary.

* *Should all these optional rights be fully exercised, and the maximum number of tons licensed be manufactured, the net additional income receivable by this Company from these royalties alone would be £21,037 per annum.*

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LECTURES.

Experimental Chemistry (Inorganic)	Prof. H. FRESENIUS, Ph.D.
Experimental Physics	W. FRESENIUS, Ph.D.
Stöchiometry	
Organic Chemistry	E. HINTZ, Ph.D.
Chemical Technology	W. LENZ, Ph.D.
Microscopy, with exercises in Microscopic work	
Chemistry and Analysis of Foods ..	Prof. H. FRESENIUS, Ph.D. / Prof. E. BORGMANN, Ph.D. / W. FRESENIUS, Ph.D., and E. HINTZ, Ph.D.
Hygiene	Dr. med. G. FRANK.
Practical exercises in Bacteriology ..	
Technical Drawing, with exercises ..	J. BRAHM.

The next Session commences on the 24th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL'S Verlag, at Wiesbaden, or to the undersigned.

Prof. R. FRESENIUS, Ph.D.

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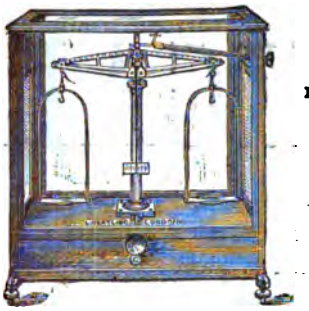

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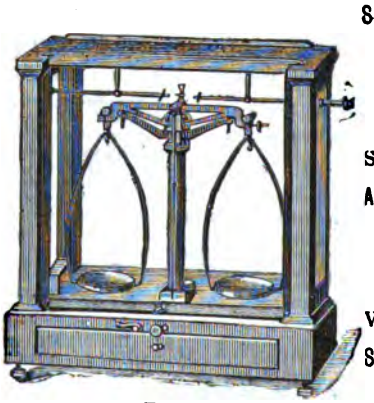

FIG. 3*a*.

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EXAMINATIONS.

Mr. Auberon Herbert's protest against Examinationism is in some respects an exceptional document. It secured the approval of eminent men who otherwise had liltle or nothing in common, and it drew forth from dissidents nothing worth calling a reply, save the query, what are we to put in the place of our examinations? This question is, we submit, illegitimate. Suppose a physician is practising unsuccessfully during an epidemic, would it not be thought strange were he to ask his patients or their friends what treatment he should substitute for that which he finds useless? But substitutes for examinations as at present are perfectly conceivable, and could be easily adopted. The amount of a man's attainments may be easily ascertained, but his capacity, his mental resources, cannot be gauged by any series of questions and shown in marks.

Still, in spite of all exposures, the game proceeds. Schoolmasters still publish the number of their pupils who have "passed;" examiners or "coaches," as distinct from professors and teachers, still flourish; cram-books adapted to some syllabus appear like flights of locusts; the examiner does not test the teachers' work—he prescribes its direction, its extent, and its quality.

Still we may hope that the Auberon Herbert manifesto has not been entirely thrown away. It is well known that the London University requires the production of some original work for the degree of D.Sc., though such research is not accepted as a substitute for the examinations, but merely as a supplement.

A more important piece of news is that the University of Oxford is about granting the degrees of M.Sc. and M.Littr. respectively for original work in Science or Literature *without* previous examinations.

The correspondence which has lately appeared in the Chemical News is a hopeful symptom. Even Dr. Tilden, who certainly has no prejudice against examinations, admits (p. 60) having given an incompetent student "5 per cent of marks *pro forma*," and thinks that such a case is not "an isolated or exceptional one." But to account for such a deplorable state of things he does not blame the system, but thinks (pp. 60 and 84) that the fault must lie either with the examiners or with their superiors.

Prof. Ramsay (p. 83) openly admits that "many students do pass" "all examinations without a competent knowledge of the subject in which they are examined," and subjoins the necessary complement, "not a year passes without my regretting that competent men have failed." In his most instructive letter he urges that the examinations should be entrusted, not, as at present, to strangers, who can judge merely from a few spoken or written answers, but to the professors or teachers themselves. These gentlemen have seen the student at work, they know his resources, and can form a fair estimate, not merely of his attainments, but of his capabilities. The same proposal is made, more overtly, by Mr. Slater, who wishes to substitute the testimony of the faculty, founded on what is really a daily examination of the student. The present system is based largely on mistrust of the teachers, as explained in Dr. Bloxam's letter (p. 95).

If examinations by strangers are deemed indispensable, they might be held, not on dates known to pupils and previously announced, but unexpectedly. Such an arrangement would greatly obviate the farce of "preparing for exams." It would, of course, be unwelcome to "coaches," since they would not be able to calculate on the subjects to be worked up, or allow for the idiosyncrasy of the examiners, whose names would not be announced.

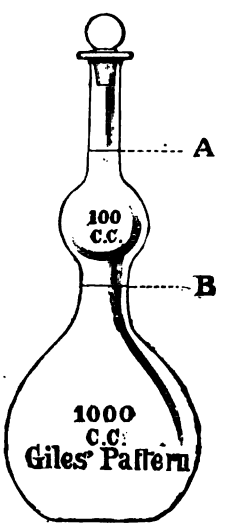
ON A MODIFICATION OF THE LITRE FLASK.

By WM. B. GILES, F.I.C.

In the preparation of solutions intended for use in volumetric analysis, it is of primary importance that the exact titre—or strength—be established before they are applied to the estimation of undetermined factors. In many cases this is effected by taking an exact weight of the reagent and dissolving it so that the solution may amount to exactly one litre in volume at the standard temperature. When this method is applied to such materials as potassium bichromate, silver nitrate, and similar reagents which are readily obtained in a state of almost chemical purity, it answers fairly well, although, to an accurate worker, it is preferable even in such cases to determine their actual reacting power by direct experiment. When, however, the nature of the reagent employed renders it difficult or impossible to obtain an exact quantity by direct weighing, a correction of the resulting standard solution becomes an absolute necessity, as is well known.

In working with such bodies as, *e.g.*, sulphuric acid, thiocyanate of ammonium, or uranium nitrate, if normal solutions are desired, they must in the first instance be prepared too strong; and, after their exact working strength has been established by experiment, they must be reduced by the addition of more fluid to the normal strength. With the ordinary litre flask this involves some difficulties. Assuming that the solution has been made up to the mark, a certain portion must be withdrawn to determine the titre, leaving an odd number of c.c. in the flask to be corrected after trial, even if a portion is poured into another smaller graduated measure, and some calculation is needed to determine the amount of fluid to be added.

Having frequently experienced this difficulty, I have devised the modification illustrated beneath. The measuring flask has an additional bulb blown upon its neck. Up to the ring marked B it holds exactly 1000 c.c. Above this is the bulb with another mark, A. Between these two marks the contents are 100 c.c. To make any normal solution with these flasks, *one-tenth more* of the reagent is weighed out than would be used with an ordinary flask, and the vessel is filled to mark A,



always taking care that the resulting solution shall be *rather too strong*. After thorough mixing, enough is poured into a clean vessel to bring the fluid to mark B; thus there is obtained 100 c.c. of solution for ascertaining the exact titre, and exactly one litre is left in the measuring vessel for correction. In this way the calculation is much simplified, and the additional space afforded by the bulb facilitates the ready mixing of the fluid.

I have also had some 2000-c.c. flasks made on the same principle. In this case the bulb holds 200 c.c.*

APPROXIMATE DETERMINATION OF THE EQUIVALENT OF RARE EARTHS BY TITRATION.

By GERHARD KRÜSS and ANTON LOOSE.

In researches on the earths of the yttrium and cerium groups, the equivalents have of late years been always determined in this laboratory gravimetrically by converting the earth into sulphate. As such investigations necessitate the execution of many hundreds of these analyses, the loss of time in such operations was greatly felt.

The most varied attempts were therefore made to determine the equivalent of the earths volumetrically with dispatch and convenience.

The most favourable results were obtained by a method of precipitation. We used as precipitant a decinormal oxalic acid, as the yttrium and cerium earths should yield neutral oxalates sparingly soluble in water and dilute acids.

For the execution of the first experiments a yttrium earth ($R^{III}=95{\cdot}8$ according to a gravimetric determination) was selected which had been previously freshly purified and finally obtained from the oxalate by slow ignition, dissolved in hydrochloric acid, and after the evaporation of the excess of acid the very faintly acid solution was made up to 1 litre. The determination of a portion by precipitation with ammonia gave for 10 c.c. 0·09075 grm. earth. 1 c.c. earth solution = 0·009075 grm. R_2O_3.

With this solution experiments were made as follows:—Portions of the solution of 20 c.c. each were put in a beaker, and the oxalic acid was carefully introduced until after heating on the water-bath and the settlement of the precipitate no further deposition was perceptible— a procedure exactly analogous to that followed in Gay-Lussac's determination of silver.

The results were as follows:—For 20 c.c. of the earthy solution, containing 0·1815 of earth, there were required of decinormal oxalic acid—

43	44
41·7	42·7
45	45·5
44·3	41·6
43	44·0

An accurate agreement, therefore, could not be obtained in this manner even on the most careful observation.

A method was therefore adopted which is almost more convenient. An excess of oxalic acid was at once added to the solution of earth, the oxalates were filtered off, and the excess of acid in the filtrate was determined by titration with permanganate.

In order to be certain that dissolved oxalate did not occasion an excess of oxalic acid in the filtrate on titration with permanganate, we ignited the oxalates after filtration and washing in a series of cases, and weighed the earths. There never appeared—if we disregard slight inevitable losses—an essential decrease in the weight of the earth taken, whence we cannot assume that the titration is appreciably affected by the solubility of the earthy oxalate.

Such titrations with oxalic acid and permanganate showed that 20 c.c. of the above-described solution of yttrium earth required for precipitation—

Decinormal oxalic acid.
C.c.
44·6
44·8
44·7
44·6
44·8
44·7
44·6

Or 44·7 on an average.

10 c.c. of the same solution required for precipitation—

Decinormal oxalic acid.
C.c.
22·2
22·3
22·3
22·3
22·4

Or a mean of 22·3

From the results of both series of experiments it follows that 44·65 c.c. of decinormal acid, or 0·2009 grm., combined with 0·1815 grm. of earth, which, if we assume the formula $Yt_2(C_2O_4)_3$, shows a $Yt^{III}=97{\cdot}8$. The determination of the atomic weight for R^{III} on the present specimen, by weighing the earth and the sulphate obtained gave the value $Yt^{III}=95{\cdot}8$.

After an approximate agreement had been reached in this case, it seemed, therefore, necessary to test the suitability of the volumetric method of determination on other materials. The following Table gives a number of experiments undertaken with earths of various composition:—

Material.	Earth in grms.	Oxalic acid in grms.	R^{III} found by analysis. Oxalate, volumetric.	Sulphate, gravimetric.
Didymium, very pure	0·1976	0·1504	153·3	145·3
,, ,,	0·1172	0·0846	153·4	145·3
,, ,,	0·1742	0·13365	151·8	145
,, ,,	0·1591	0·126	146·4	138·8
Yttrium	0·0384	0·0342	127·5	119·5
,, ...	0·4084	0·0466	94·2	92
,, ...	0·1075	0·09675	126·0	118·4
,, ...	0·3662	0·3352	104·1	97·1
,, ...	0·2956	0·2972	110·2	102·5
Terbium	0·1747	0·1225	168·3	157·5
Holmium	0·1608	0·10818	176·4	165·5
,, ...	0·3354	0·2367	167·1	158·5
Erbium	0·1380	0·09135	179·7	168·5
,, ...	0·234	0·15705	177·0	163·4
Erbium containing ytterbia	0·0615	0·0393	187·2	166·7
Ytterbium	0·0504	0·0288	212·2	173
,, ...	0·369	0·22275	199·5	169·3

We see that in this conspectus only the value found for the relatively purest yttrium substance corresponds approximately with the real atomic weight found gravimetrically by the sulphate method, whilst the other results show more important deviations. This is the more striking as previous statements on the oxalates of the rare earths regard them as neutral salts.

According to the above results the values obtained by titration all appear too high. Hence more earth than is

* These measuring flasks were made for me by Messrs. Baird and Tatlock, who keep a stock of them.

required to form a neutral oxalate must be combined with each quantity of oxalic acid. Thus we have in part feebly basic compounds.

If we consider the didymium substance which is first mentioned in the above Table, its equivalent amounts according to the volumetric determination: Di = 51·1 (corresponding to R^{III}=153·3) instead of 48·4 or R^{III}= 145·3. The difference in the equivalents in this case is almost 3 units.

If we multiply the value 51 by 16 we obtain a product which approximately represents 17 equivalents, whence it would follow that under these experimental conditions there would be formed an oxalate containing 17 equivalents of the rare earthy metal and 16 equivalents of oxalic acid. If, on the assumption of the formation of such a basic oxalate we calculate the results of the above titrations by multiplying the R^{III} values obtained by 16/17, we obtain the following values:—

Substance.	Atomic weight after determination gravimetrically as sulphate.	Atomic weight from volumetric data.
Didymium, very pure	145·3	144·3
,, ,,	145·3	144·3
,, ,,	145·0	142·8
,, ,,	138·3	137·8
Yttrium	119·5	120·0
,, ...	92·0	88·7
,, ...	118·4	118·5
,, ...	97·1	98·0
,, ...	102·5	103·7
Terbium	157·5	158·4
Holmium	165·5	166·0
,, ...	158·5	157·2
Erbium	168·5	169·1
,, ...	163·4	166·6
,, containing ytterbium	166·7	176·2
Ytterbium	173·0	199·7
,, ...	169·3	187·8

It is plainly to be seen that the cerium and yttrium earths agree approximately with the above proportion. The proportion 17 : 16 is approximately equal to 1 : 1, whence the representation of the oxalates of those rare earths as neutral salts is intelligible. It must also be remembered that these oxalates were formerly analysed chiefly by determining simply, in a given weight of substance, the earth and the crystalline water without executing a combustion. The determination of the crystalline water is, however, greatly impeded because, according to all authorities, the last traces of crystalline water do not escape until a decomposition of the oxalic acid sets in. It is possible that this analytical difficulty may in some cases have led to incorrect formulæ for the composition of the oxalates.

Departures from the composition of a 17/16 basic earthy oxalate are, according to the above determinations, recognised in the oxalates of the pure yttrium substance (R^{III}= 92) and of ytterbia. If yttria is pure the composition of its oxalate seems to approach that of a neutral salt, whilst ytterbia seems to form a more basic oxalate than the other earths, whence the values found for ytterbium by titration are considerably too high.

Closer examinations on the composition of the oxalates of the rare earths are in course of execution in this laboratory.

Although the above volumetric determination of the equivalents of the yttria, &c., earths can by no means claim to supersede the gravimetric determination of the equivalent of the earths we may in this manner quickly arrive at approximately accurate results, especially if we take into account the formation of basic salts as above.

Determinations of the equivalents in working with rare earths are almost exclusively undertaken only for a preliminary view of the material. If, *e.g.*, it is required to ascertain quickly whether in a series of fractions the atomic weights are rising, falling, or remaining constant, the present method of titration is especially suitable, as the author has convinced himself by special trials. For accurate determinations we must then return to the more exact gravimetric method.

Finally, for the successful execution of titrations on the above method it is recommended to add to the solution of the earth, which must not be too strongly acid, the smallest possible excess of decinormal oxalic acid, which is titrated back with permanganate.—*Zeitschrift Anorg. Chemie*, iv., 161.

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

SECOND PAPER: THE ANALYSIS OF BARIC CHLORIDE.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 92.)

Ratio of Baric Chloride to Baric Sulphate.

IT is well known that such a ratio as that of baric chloride to baric sulphate could form at best but a very poor basis for determining the atomic weight of barium (Ostwald, "Allgemeine Chemie," i., 23; *Proc. American Academy of Arts and Sciences*, xxviii., 11). An experimental error in the process is necessarily magnified many times when referred to the constant sought. Nevertheless, since five distinguished chemists have tried this method, it was thought expedient to attempt it, in order to show if possible the cause of the great discrepancies in their results.

The investigation of the ratio occupied several months, but the report of it will be greatly abbreviated. The principal cause of error was found in the very decided occlusion of baric chloride by baric sulphate, a fact which has already been discussed in a previous paper (*Proc. Amer. Acad. Arts Sci.*, xxvi., 258). This cause of error was never wholly avoided, although by repeated treatment of the baric sulphate with sulphuric acid, all but a few tenths of a m.grm. of chlorine were found to be expelled. Whether or not the baric chloride is occluded in the form of a so-called "solid solution," as A. E. Schneider suggests in a recent paper with regard to the occlusion of ferric sulphate by baric sulphate (*Zeit. für Physikal. Chem.*, 1892, x., 425), the fact remains that an appreciable amount of baric chloride is very firmly held. Possibly nothing short of the true solution of all the baric sulphate in sulphuric acid could drive off all the chlorine; and such treatment would be likely to introduce errors as large as the one which it would obviate.

Besides this inclusion of baric chloride, which tends to raise the apparent atomic weight of barium, another circumstance, the solubility of baric sulphate in water, may work in the same direction. This second cause of error was quite eliminated in the present work. A third cause of error with an opposite tendency exists; namely, the obstinacy with which baric sulphate retains the last traces of the excess of sulphuric acid and water used to precipitate it. It must be borne in mind that the retention of 0·2 m.grm. of either substance counterbalances numerically the retention of nearly 2 m.grms. of baric chloride.

Two series of determinations were made, one by the direct addition of pure sulphuric acid to a concentrated solution of pure baric chloride in a platinum crucible, the other by precipitation in dilute solution after the usual fashion. In the latter case the baric sulphate in the filtrates, usually amounting to about 1½ m.grms., was determined by evaporation in large platinum dishes. In each series every specimen of baric sulphate was of course heated with successive drops of pure sulphuric acid at a dull red

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*.

heat until the weight became constant. Eight experiments which were not complicated with mechanical errors are recorded in the note book. The two series gave the same result, 100 parts of baric chloride yielding 112·073 parts of baric sulphate. The highest result was 112·087, and the lowest 112·060. Berzelius found 112·175, Turner 112·19, Thomson about 112·15, Struve 112·094, and Marignac 112·011.

Owing to the chemical errors which have just been pointed out, the results given above are of no real value. For this reason the individual data are omitted. The uncertainty of the result 112·073 is probably as much as a unit in the second decimal place; therefore the atomic weight of barium computed from it, 137·43, cannot be relied upon to within 0·2. The different errors tend to eliminate one another, so that the result is by chance near the true one.

Solubility of Argentic Chloride.

Since it is evident that no satisfactory results are to be obtained from the ratio just discussed, the careful investigation of the ratios of silver and argentic chloride to baric chloride assumes even greater importance than before.

The solubility of argentic chloride is the most serious difficulty which is to be overcome in this investigation. Gay-Lussac knew that the filtered liquid which remains after mixing equivalent amounts of solutions of argentic nitrate and a chloride invariably gives a precipitate with an excess of either reagent, showing that some argentic chloride must remain in solution. Mulder, in 1857 (Mulder, "Essayeer-Methode van het Zilver," Scheikundige Verhandelingen en Onderzoekingen, 1 Deel, 1 Stuk, 1857; translated by Grimm, "Die Silberprobirmethode," Leipzig, 1859), recognised very clearly the same fact, and pointed out, with the help of a great number of detailed experiments, just what influence this fact has upon the titration of silver by Gay-Lussac's method.

Mulder wrongly ascribed the solubility of argentic chloride to the presence of the alkaline nitrate resulting from the decomposition, for he believed that the curdy precipitate was wholly insoluble in pure water, or in water acidified with a reasonable amount of nitric acid. Six or eight years later Stas ("Untersuchungen," &c., translated by Aronstein, Leipzig, 1867, pp. 46, 56, 59, and 295), without knowing of Mulder's work, clearly recognised the difficulty, but fell into serious blunders in interpreting it. Before 1872, however, when his noted researches on the "chemical statics" of argentic chloride and bromide began to appear (*Annales de Chim. et de Phys.*, 4th Series, xxv., 22; and 5th Series, iii., 145 and 289), he had become familiar with Mulder's work, and had adopted many of his points of view.

In these last researches Stas found that freshly precipitated voluminous argentic chloride was soluble to a very large extent (over 10 m.grms. to a litre) in the purest water, and that nitric acid or the alkaline nitrates had no appreciable effect upon the solubility. The pulverulent precipitate obtained by continual shaking he found to be much less soluble, only 0·7 m.grm. being dissolved by a litre of pure water. Nitric acid increases to a sensible degree this last quantity, the increase being approximately proportional to the amount of acid present.

Mulder knew well that it was possible wholly to precipitate either silver or chlorine by the addition of a sufficient amount of the other reagent, but wrongly assumed that the amount of the reagent required was a direct measure of the solubility of argentic chloride. This misconception probably arose from a theoretical discussion of very doubtful value; its effect was to make Mulder's estimate of the solubility rather excessive. Stas recognised the fact for the first time, that much more silver is required to precipitate the chlorine in solution as silver chloride than is enough directly to combine with it. A very tedious series of experiments led him to the conclusion that for every molecule of argentic chloride dissolved just 3 molecules of argentic nitrate or of a chloride were required to complete the precipitation. In 1881 Cooke called attention to some of the same facts.*

Much time has been spent during the present research upon the subject, for its importance with regard to the analysis of baric chloride was very evident. The experiments were largely a repetition of Stas's, with occasional variations suggested by the case in hand. Mulder and Stas having wholly done away with the old idea of the insignificance of the action of light on the haloid compounds of silver, the greatest care was taken with regard to the protection of the precipitates from diffused light. Work with them was performed wholly in a dark room lighted by means of illuminating gas shining through thick orange glass; and even here the flasks were always covered by two or three thicknesses of black cloth when left to themselves.

In determining the solubility of argentic chloride a number of experiments were made, first by colorimetric and "opalimetric" methods. The colouration produced by hydric sulphide and the opalescence produced by hydrochloric acid were compared with similar phenomena produced by known amounts of silver. Very much experience is needed to obtain satisfactory results with either of these methods, so that a more direct method of determination was sought.

An opalescent solution produced by the addition of hydrochloric acid or argentic nitrate to a solution of argentic chloride often requires many weeks to deposit its suspended salt, even when warmed and shaken, if the flask is kept wholly in the dark. The effort to evaporate the solution by boiling in vessels partially closed to exclude the dust, proved equally unsatisfactory. Hence in order to weigh very small amounts of dissolved argentic chloride it was necessary to evaporate the solution upon the steam-bath in suitably protected glass dishes. In order to determine the magnitude of any possible errors which might arise from this method of treatment, a number of check experiments were made. In the first place dilute solutions of argentic nitrate were evaporated to small bulk with the addition of nitric acid. The evaporated solution was filtered through a small paper, and the ash of the washed filter was dissolved in nitric acid and titrated with a weak standard solution of ammonic sulphocyanate (see *ante*, "Standard Solutions"), after the method of Volhard. Three experiments showed that an amount of silver equal to about 0·02, 0·01, and 0·00 m.grm. respectively had been retained by the filter. These experiments proved that the precautions taken to prevent dust or foreign materials from reaching the surface of the solutions during the process of evaporation had been sufficient for their purpose; also, that no very important amount of silver was held by the paper.

Having determined these facts, the next step was to determine whether all of a very small known amount of argentic chloride could be recovered. A few preliminary experiments showed that in order to reduce and recover all the silver by the ignition of the filter paper, it was necessary to keep the precipitate in a finely divided state. This end is easily accomplished by using a solution dilute enough to prevent the clotting of the opalescent chloride. Thus 1 c.c. of the weak standard hydrochloric acid precipitated enough argentic chloride from a slight excess of the nitrate to require after reduction by the burning of the filter 0·97 and 0·99 c.c. of the sulphocyanate solution. Although the evaporation was conducted in dull diffused light, the argentic chloride was not discoloured (compare *Pohl. Jahresbericht*, 1851, p. 369; quoted by Mulder, "Silberprobirmethode," p. 19). These experiments showed that a small amount of argentic chloride could be nearly all recovered from a small volume of solution.

The next experiments were made with large volumes of solutions containing about 0·2 grm. of silver, a very little baric nitrate, and a small amount of nitric acid, besides

* *Proc. Amer. Acad. Arts Sci.*, xvii., 7. Cooke also studied the action of hot water upon argentic chloride.

the measured amount of standard hydrochloric acid. Two experiments, after filtration, ignition, and titration as before, indicated that 1·01 and 1·02 m.grms. of silver were precipitated by 1 c.c. of hydrochloric acid, instead of just 1 m.grm. Again, with all the other conditions just the same, 0·50 c.c. of hydrochloric acid precipitated in two cases 0·62 and 0·59 m.grm. of silver. In order to determine whether the presence of large amounts of baric nitrate might make any essential difference, these experiments were repeated with the addition of 5 grms. of the purest preparation of this salt (*Proc. Amer. Acad. Arts Sci.*, xxviii., 16, 19), quite free from chlorine. In this way 0·50 c.c. of hydrochloric acid yielded 0·57 m.grm. of silver and 0·20 c.c. precipitated 0·27 m.grm. of silver. The last six experiments showed that the presence of a considerable excess of silver in solution causes the precipitation of a slight excess of silver with the chloride.

Two experiments with neutral solutions treated in the same way showed much more marked gains; one exposed to the air during evaporation for eight hours gained 0·13 m.grm of silver; and the other, evaporated for twenty-four hours, the water being replaced from time to time, gained 0·32 m.grm. These gains might have been due to the action of organic matter in the absence of nitric acid, or the action of alkali dissolved from the glass; in any case, the necessity of the presence of free acid was shown.

In the work which follows it was several times necessary to evaporate strongly acid solutions of argentic chloride containing only a very slight excess of silver, hence parallel determinations under these conditions were very essential. In this way three successive experiments yielded respectively 0·38, 0·38, and 0·37 m.grm. of silver, instead of 0·50 m.grm., which should have been obtained; one experiment gave 0·52 instead of 0·60, and two more gave respectively 0·90 and 0·93, instead of 1·00. Hence, when much nitric acid and very little silver are present the amount of metal found is too small instead of too great.

These determinations all together show that the evaporation of solutions of argentic chloride upon the water bath is a process carrying with it small errors, some plus and some minus, which are reasonably constant under constant conditions. They show also that the presence of baric nitrate does not in the least alter the accuracy of the determination, which depends chiefly upon the relative amounts of argentic nitrate and nitric acid present in each case. They moreover furnish a means of correcting results obtained by the method in hand. A solution containing two-tenths of a grm. of argentic nitrate, 3 grms. of nitric acid, and a very small known amount of argentic chloride, evaporated for four or five hours, yields about 0·00006 grm. too much silver, and a similar solution containing only a few m.grms. of argentic nitrate yields about 0·0001 grm. too little. The bearing of these facts upon the subject will presently be made more evident.

It was now possible to determine the solubility of argentic chloride less crudely. Half a litre of the purest water, after being shaken occasionally with the purest argentic chloride for two hours, yielded 0·50 m.grm. of silver, and a similar preparation, which had been allowed to stand for twenty-four hours with more frequent shaking, yielded 0·60 m.grm. The solubility of this argentic chloride is thus found to be about 1·5 m.grms. per litre. The result is not far from the mean of the colorimetric tests.*

To determine the influence of nitric acid upon the solubility, 4 grms. of this substance were added to over a litre of pure water, and the mixture was shaken with the same argentic chloride. 300 c.c. of the solution yielded 0·47 m.grm. of silver, and two portions of 400 c.c. each yield 0·56 and 0·57 m.grm. of silver respectively. After adding the appropriate correction, and taking the mean of these determinations, the solubility is found to be about 2·3 m.grms. per litre.

In a number of analyses exactly equivalent amounts of baric chloride and argentic nitrate in dilute solution were shaken together, and both chlorine and silver were determined in the filtrate. These analyses were primarily to determine the atomic weight of barium, and will be described later; but since the chlorine was found to be present in the filtrate in amounts almost exactly equivalent to the silver, they may be used also to measure the solubility of argentic chloride in solutions containing about 2·5 c.c. of nitric acid, and 3 to 8 grms. of baric nitrate. In one case, where the solution had been shaken with the argentic chloride for ten days, the solubility was found to be about 1·6 m.grms. per litre; in another, violently shaken, but allowed to stand for a shorter time, it was found to be about 1·7 m.grms. per litre; and in a third, much less violently shaken, but allowed to stand for a week, it was as much as 2·7 m.grms. per litre. In each of these cases the temperature was about 20°.

These results are, as one would expect, between the limits set by Stas; for the precipitate was in the state usually observed, having lost its first flocculence, and not having been wholly converted into powder.

A careful series of experiments was made to confirm Stas's statement that the chloride is absolutely insoluble in water containing an excess of argentic nitrate. It is not needful further to describe these experiments, except to state that the confirmation was wholly satisfactory. In the course of this work I was able to detect repeatedly one part of chlorine in thirty million parts of water, by careful comparison in strong sunlight after treatment with excess of argentic nitrate. The very faint opalescence of course very soon disappears, owing to the blackening of argentic chloride by the powerful light.

(To be continued).

* It is noteworthy that Kohlrausch and Rose have found the solubility of argentic chloride to be 1·52 m.grms. per litre at 18°. This determination was based upon the electrical conductivity of the solution. (*Zeit. Physikal. Chem.* xii., 234.)

THE ACTION OF HEAT UPON ETHYLENE.*

By VIVIAN B. LEWES.

(Continued from p. 89).

In the following set of experiments the ethylene, after purification from oxygen by standing over a dilute solution of sodic pyrogallate and sodic hydrate, was passed through the tube at the rate of about 10 c.c. per minute. (See Table I.).

These experiments are of considerable interest, as they throw some light upon the changes taking place during the heating of ethylene.

The gas being passed through 140 m.m. of heated tube, no change takes place until a temperature of 800° C. is reached, when traces of acetylene are observed; between 800° and 900° C. the acetylene increases in quantity, and large quantities of methane are generated, accompanied by liquid products. This action increases until just below 1200° C., when hydrogen begins to appear amongst the products of decomposition, whilst the moment the liberation of hydrogen commences, carbon also is deposited; and the formation of oil decreases until close upon 1500° C., when the decomposition of the ethylene is practically complete, and the products of decomposition are mainly hydrogen with some undecomposed methane, and a copious deposit of carbon.

In each experiment the products of decomposition were examined to see if any member of the C_nH_{2n+2} group other than methane was present, and in no case could any be detected. This seems to point strongly to the conclusion that the ethane formed in the previous experiment, in accordance with the experiments of Day and Berthelot, had its origin as a secondary, and not as a pri-

* A Paper read before the Royal Society.

TABLE I.—*The Action of Heat upon Flowing Ethylene.*

Percentage of ethylene in original gas ..	96·78	96·78	96·78	94·8	98·91	98·91
Temperature of gas in decomposing tube	600° C.	700° C.	800° C.	900° C.	1000 C.	1200° C.	1500° C.
Analysis of Gas after heating, per cent.							
Unsaturated hydrocarbons	96·42	96·39	96·46	34·77	18·02	10·54	0·43
Containing acetylene	0·00	0·00	trace	0·82	0·60	3·60	0·00
Saturated hydrocarbons	0·00	0·00	0·00	59·73	76·48	55·26	27·80
Hydrogen	0·00	0·00	0·00	0·00	0·00	25·11	62·68
Carbon deposited and Oil formed, in grms. per 100 c.c.							
Carbon	0·00	0·00	0·00	0·00	0·00	0·0273	large quantity
Oil	0·00	0·00	0·00	0·0024	0·0048	0·0038	0·00
Change of volume	none	none	none	decrease	decrease	increase	large increase

mary, product of decomposition, but it was clear that to determine this point other experiments must be made, to see if under these conditions of temperature a slower rate of flow was attended by generation of any saturated hydrocarbons higher than methane.

In order to do this, the same arrangement of apparatus was employed, but the rate of flow of ethylene was diminished to 4·2 c.c. per minute, the gas, after heating, being collected as before, and an analysis made, in which the saturated hydrocarbons were calculated from the results of the paraffin absorption and subsequent explosion. A second analysis was then made of the heated gas without any paraffin absorption, and the volume of carbon dioxide formed on explosion calculated as methane. If the volume so obtained is found to be greater than that originally given by the combined paraffin absorption and subsequent explosion, it is held to be evidence that some higher member of the paraffin series must be present. In order to ascertain if any unsaturated hydrocarbon other than ethylene is present in the gas after heating, a sample of the gas being exploded with oxygen, and the carbon dioxide estimated; should the amount formed exceed the carbon dioxide calculated from the second analysis, it may be taken as evidence that an unsaturated hydrocarbon higher than ethylene is present.

Analysis of the Ethylene used in these Experiments.

Carbon dioxide	Nil
Oxygen	0·24
Ethylene	98·55
Nitrogen	1·21
Methane	Nil
Hydrogen	Nil
	100·00

These experiments show conclusively that when only flowing slowly through the tube a higher member of the paraffin group, probably ethane, is formed up to 900° C., whilst at 1000° C. the quantity has rapidly diminished, and at 1200° C. methane is the only member of the series present.

In the same way a small trace of some unsaturated hydrocarbon, probably benzene, is present at the lower temperatures, but disappears when 1200° C. is reached.

The next step was to see if the action of heat upon ethane under the same conditions as those existing in the previous set of experiments bore out the results arrived at.

Ethane was prepared by acting on ethyl iodide with a copper-zinc couple in presence of water, and passing the evolved gas through fuming sulphuric acid to purify it.

TABLE III.—*The Action of Heat upon Flowing Ethane.*

Percentage of ethane in original gas	96·38	96·38	96·38	96·38
Temperature of gas in the decomposing tube	900° C.	1000° C.	1200° C.	1500° C.
Analysis of the gas after heating—				
Unsaturated hydrocarbons	31·00	28·42	11·58	1·69
Containing acetylene	trace	0·30	1·80	0·91
Saturated hydrocarbons—Paraffin ..	12·82	8·34	3·88	0·00
Methane ..	12·01	12·73	21·86	20·62
Hydrogen	40·64	46·78	57·45	73·35
Carbon deposited and oil formed in grms. per 100 c.c. of gas—				
Carbon	0·0	0·0	0·0126	0·0314
Oil	0·0	trace	trace	0·0

TABLE II.—*The Action of Heat upon Ethylene Flowing at the Rate of 4·2 c.c. per Minute through 6 in. of Heated Tube.*

I. Analysis of Heated Gas made with Paraffin Absorption and Explosion.

Temperature of gas in tube	800° C.	900° C.	1000° C.	1200° C.
Unsaturated hydrocarbons	91·90	84·31	45·31	18·31
Saturated hydrocarbons—				
By paraffin	1·63	5·00	6·71	4·56
By explosion	0·60 } 2·23	1·48 } 6·48	23·40 } 30·11	24·01 } 28·57
Hydrogen	3·26	4·67	19·65	49·51
Carbon monoxide	1·11	1·40	1·23	1·10
Carbon dioxide	nil	nil	nil	nil

II. Analysis of Heated Gas made without Paraffin Absorption.

Unsaturated hydrocarbons	92·0	84·15	45·72	18·20
Methane calculated from CO_2	4·1	10·25	34·11	28·79
Carbon monoxide	1·2	1·50	1·28	1·0

III. Carbon Dioxide from Total Explosion.

Calculated from Analysis II.	189·3	180·7	129·2	69·31
Found	190·0	182·4	133·4	69·00
Carbon deposited in tube, grms. per 100 c.c. of gas	trace	trace	0·0101	0·2150
Oil formed per 100 c.c.	0·012		0·0573	0·0035
Vol. of gas before heating	521·7	lost	514	350
Vol. of gas after heating	469·1		460	470

These results show that, even below 900° C., ethane decomposes with liberation of hydrogen and formation of unsaturated hydrocarbons, which on examination prove to consist of ethylene with small quantities of acetylene, rise of temperature completing this decomposition, and also causing the ethylene to decompose as before.

It is evident that, if ethane had been a primary product in the decomposition of ethylene, it would in turn have decomposed with liberation of hydrogen at or below 900° C., and hydrogen would have been found at that temperature as a product of the decomposition of the ethylene, instead of its appearance being coincident with the deposition of carbon at 1200° C.

The fact that with a rapid flow I was unable to detect a trace of free hydrogen until carbon has begun to deposit, or *vice versâ*, shows the fallacy of the text-book equation $C_2H_4=CH_4+C$, and on examining the evidence upon which the statement is based, we find that Marchand (*Journal fur Prakt. Chemie*, vol. xxvi., p. 478), who originated it, passed ethylene through glass and earthenware tubes heated to redness, and analysed the resulting products by passing them over heated copper oxide, and estimating the carbon dioxide and water vapour formed. At first the proportion of carbon to hydrogen was 100 to 17·236, which corresponds to nearly pure ethylene, and on heating to a higher temperature the ratio altered to 100 carbon to 30·771 hydrogen, which nearly corresponds to methane, carbon being at the same time deposited; but this is manifestly no proof of the gas being methane, as a mixture of undecomposed ethylene and hydrogen, or mixtures of ethylene, methane, and hydrogen, such as those formed at 1200° C., would give the same result.

His results were to a certain extent confirmed by Buff and Hofmann, who noticed that when the platinum spiral was heated in pure ethylene there was at once a deposition of carbon, whilst the gas scarcely expands, from which they concluded that methane had been formed at the same time. When, however, the experiments tabulated in Table I. are examined, it will be seen that as soon as 1200° C. is reached and carbon is deposited expansion takes place; but that at all temperatures short of that there is contraction due to some of the gaseous products undergoing polymerisation and yielding liquids. In Buff and Hofmann's experiment the gas in contact with the incandescent wire was decomposed with liberation of hydrogen and separation of carbon; but the expansion caused by this action happened to be nearly equalised by the contraction due to polymerisation in the less heated portions of the gas.

The simultaneous appearance of carbon and hydrogen indicates clearly the liberation being due to the splitting up of a hydrocarbon, and the proportion in which these elements are liberated point to acetylene as being the body concerned.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 23rd, 1894.

Prof. A. W. Rücker, M.A., F.R.S., President, in the Chair.

Mr. J. W. Kearton was elected a member of the Society.

A "*Note on a New Electrical Theorem*" was read by Mr. T. H. Blakesley, M.A. M.Inst.C.E.

Two or more dispositions of electromotive forces in any network of conductors which produce at every part of the network the same currents are defined as *equivalent systems*. The following theorem is then stated and proved:—

In any system of conductors possessing seats of electromotive force at any number of points, if any of these sources be moved along the various bars of the inducting system, and where a point of junction is encountered, each becoming a seat of the *same* electromotive force in *each* of the newly encountered bars, then the disposition at any moment is equivalent to that at any other moment, and therefore to the original disposition. Equivalent systems might also be defined as being such as produce equal expenditure of power in each part. From the above theorem the following propositions are deduced by the author:—1. That if any closed surface contains a portion of a network, then an electromotive force in any bar cutting the surface can be replaced by equal electromotive forces (in opposite directions as regards the surface) in all the other bars cutting the surface, without disturbing the current in any part of the network. 2. If two systems of electromotive forces be equivalent, one may be derived from the other.

Prof. C. V. Boys, F.R.S., read a note on the "*Attachment of Quartz Fibres.*"

When torsion fibres are required to carry large weights approaching the breaking weight, the ordinary method of attachment by shellac is not always satisfactory; for if the part of the fibre in the cement is twisted or bent, the yielding of the shellac causes uncertainty of zero. To avoid these troubles, Prof. Boys has devised and perfected a method of soldering the fibres, full details of which are given in the paper.

After selecting a fibre of the right diameter and length, small weights are fixed in the ends by shellac. The end parts are then cleaned by dipping in strong nitric acid, washed, silvered, and electro-coppered. The weights are then cut off and the coppered ends soldered to tags of tinned metal foil, chloride of zinc being used as a flux; and its capillarity serving to hold the ends to the tags whilst the latter are heated. The superfluous copper and silver are dissolved off by nitric acid, the tags and solder being meanwhile protected by bees'-wax. After washing in boiling water the fibre is ready for use. Melted shellac is used for securing the tags to the torsion rods and suspended body. Several ingenious details of procedure to avoid capillary difficulties in the cleaning, plating, and washing processes are described in the paper. If fibres are required to conduct electricity, they are silvered and washed after the tags have been soldered on. Such fibres the author considers essential for making connection with electrometer needles of the greatest delicacy; for liquid connections are fatal to stability. Methods of rendering fibres visible by smoking with arsenic or magnesium are mentioned in the paper.

At the meeting a perfectly circular hole $\frac{1}{1000}$th of an inch in diameter, made by soldering round a quartz fibre passing through a hole in a metal plate and then drawing out the fibre, was exhibited under a microscope.

Mr. Inwards asked if the shellac used to secure the tags was melted or dissolved.

Mr. Blakesley enquired if silvering fibres did not destroy their perfect elasticity.

Dr. Sumpner wished to know if any data as to the relative torsional rigidity of silvered and unsilvered fibres had been obtained, and if the electric resistance of silvered fibres had been determined.

Mr. Watson said silvered fibres had been successfully used in electrometers. As regards their torsion, he had found it differ from day to day, and the resistance varied enormously.

In reply to a question, Prof. Boys described the exact process of soldering the coppered fibre to the tags. As to the torsion of silvered fibres, he would not expect much increase as the film was very thin. He also thought the elasticity would not be destroyed, for silver and gold make very good torsion wires.

Mr. Littlewood read a note on "*A Method of Determining Refractive Indices*," particularly well adapted for either homogeneous or heterogeneous liquids.

A vertical scale stands in the liquid contained in a vessel open at the top, and two marks on the part of the scale below the liquid are observed in succession through an inclined telescope capable of moving horizontally parallel to itself along a graduated bar. The horizontal distance between the two positions of the telescope in which the two divisions on the vertical scale are sighted is noticed, and the corresponding distance between the sighted position of the marks on the part of the scale above the liquids determined. When the length between the two marks on the scale in air is equal to that between those in the liquid, the ratio of the corresponding horizontal distances moved through by the telescope gives the index of refraction of a uniform liquid. For liquids in which the density varies in a vertical direction, observations of several points on the scale in the liquid enable the curved path of the light in the liquid to be traced out with considerable accuracy. The accuracy of the laws of diffusion might be tested in this way.

The PRESIDENT said the method described was a novel and interesting way of picking out the layers of liquid of different refracting power.

NOTICES OF BOOKS.

Principles and Practice of Agricultural Analysis: A Manual for the Examination of Soils, Fertilisers, and Agricultural Products. For the Use of Analysts, Teachers, and Students of Agricultural Chemistry. By HARVEY W. WILEY, Chemist to the U.S. Department of Agriculture. No. 1. Easton: Chemical Publishing Co.

WE have here the first part of what promises to be a comprehensive and thorough-going work. The author does not begin with routine directions for the recognition and determination of the various constituents of plant food. He sets out with a consideration of the origin of soils and their chemical elements, those of the chief importance being particularly described. There is a special account of the probable origin of the phosphate beds of Florida, which differ remarkably from those of the West Indies in the comparative absence of iron and aluminium. He considers, with Eldridge, that they have been formed from the remains of birds and of aquatic animals deposited in the marshes.

Nitrogen, and especially the deposits of guano and of alkaline nitrates, are carefully studied. He seems to accept the theory of Nöllner that the beds of Atacama are of modern origin, and are due to the decomposition of sea plants. This is supported by the presence of iodine and absence of calcium phosphate.

He accepts boron as a "true plant food," as it is regularly present in the ash of many plants. But the same evidence may be adduced in favour of copper and manganese.

The Stassfurt potash beds he explains by the hypothesis that the lagoons from which the beds of carnallite have been deposited must have been exceptionally rich in potassium.

Mr. Wiley quotes Prof. F. W. Clarke's table of the relative abundance of the chief constituents of plant food in the air, the sea, and the solid crust down to the depth of ten miles. We are struck with the small proportion of the elements which limit the quantity of animal—and especially of human—life: phosphorus 0·09 per cent and nitrogen 0·02 per cent! In view of these hard dry facts, how laughable appear the fancies of those who assert that the earth might support a population of a thousand billions as well, as it now does, a thousand millions. Technically and commercially speaking, deposits over the chief part of the globe cease to be available long before we reach the line of ten miles below the level of the sea.

The chapter on rocks and rock-decay is exceedingly valuable. We are rightly reminded that "the full value of a chemical analysis of any rock or soil cannot be ascertained unless such an analysis is accompanied by a microscopical examination. It is desirable to know not merely what there is in any soil, but in what form these compounds exist." It is recommended, in the examination of rocks, that the material should be cut into thin slips from 1-500th to 1-600th of an inch in thickness, and examined microscopically with polarised light. Several figures of such laminæ—micrograms, as the author conveniently calls them—are here given.

Mr. Wiley divides rocks into four chief groups: aqueous, æolian, metamorphic, and igneous eruptive. Among the æolian deposits the author makes no mention of the desert sands, which are now recognised as produced, not by the action of seas or rivers, but from that of winds acting upon exposed surfaces.

It is here suggested that the metamorphosis of rocks is more rapid in low than in high latitudes. A striking instance to the contrary is to be found in Egypt.

The part played in the disintegration and decomposition of rocks by animal and vegetable life will be discussed in the next following part, to which we look forward with a lively interest.

Minutes, Reports, Papers, and Discussions of the Forty-first Annual Meeting of the American Pharmaceutical Association, held at Chicago, August 14th to 20th, 1893. Philadelphia: American Pharmaceutical Association.

THIS volume contains very much of profound interest to thoughtful men, even not connected with the pharmaceutical profession. It contains many lessons to be digested by all persons who take an interest in the advancement of Science and in higher education.

Mr. Fennel, the chairman of the Section on Scientific Papers, remarks in his Inaugural Address: "We must confess that we have few men of leisure or men of very eminent learning." But why? America abounds in men of great wealth, who, if so disposed, might be men of leisure and have the necessary opportunities for the profound study of science. Why do they persist in heaping up million upon million?

A brief but interesting paper treats of the meat extracts favoured by the American public. Unfortunately, the qualities discussed are, save that of Liebig, unknown in Britain, and the brands so much advertised here are not mentioned.

Next comes a discussion on atomic weights, in which the "so-called differentiation of one element into another" is treated by the speaker, Dr. Hinrichs, with scant courtesy. The results of Stas are pronounced erroneous, and although the name of Prout is not mentioned, a leaning to his law is unmistakable.

An extended and illustrated paper on the refractometer merits attention.

Dr. R. L. Dohme read a paper on the commercial varieties of opium and gave some facts which the anti-opium agitators in England will find very indigestible.

It appears that the two Chinese Provinces of Szechuan and Yunnan alone produce more opium than all India, and that the Chinese, in addition to their home-produce, consume nearly all the growth of India and Persia.

Dietetic experiments on imperfectly known substances are perilous. "A female student in one of our classes bit into a cashew-nut and was badly poisoned. Cardol, an acrid oil contained in *Anacardium orientale*, is dangerous even to touch." The writer submits that such substances should not be given to candidates to be identified.

Curious answers seem to be sometimes obtained at examinations. One tyro declared that the standard of English weights and measures is "the inch, taken from a pendulum ticking seconds at the bottom of the sea." Another, on being asked if air is a chemical compound or

a mechanical mixture, and of what it is composed, declared that "air is an insoluble substance in aqueous solution!" Doubtless these answers could be matched at English examinations.

We are glad to see that the members of the pharmaceutical profession, like their colleagues in the rest of the civilised world, excepting England, speak of themselves by appropriate and unexceptionable names. We find them here designated apothecaries—as in Germany—or pharmacists, as in France. It is, we suppose, too much to hope that this good example will ever be followed in England.

Legislation on the question of quack medicines, or "proprietary articles" as they are euphemistically called in America, was suggested in a somewhat half-hearted manner, but no definite tangible conclusion was reached. The nostrum business being apparently more rampant beyond the Atlantic than with us, a better conclusion could scarcely have been expected. The suggestion that before a special medicine was licensed for sale its quantitative composition should be made public and stated on the label of each package met with objections.

There was no small amount of idle talk anent the sale of poisons. It was even proposed that the sale of the ordinary mineral acids should be placed under red-tape restrictions. This insane notion for the obstruction of chemical research and chemical industry has from time to time cropped up in Britain. But for the present the anti-scientific zeal of our rulers seems to have been glutted with the addition of coal-naphtha to methylated spirit. Strangely enough the anti-poison agitators say not a word against the common, unrestricted sale of revolvers and ammunition, the legitimate uses of which are almost infinitely fewer and more trifling than those of poisons!

Studies from the Physical and Chemical Laboratories of The Owens College. Edited by Professor A. Schuster and Professor H. B. Dixon. Manchester.

The bulk of the papers contained in this volume, giving the results of some of the investigations carried on in the above-mentioned laboratories during the past few years, have been already printed in the *Transactions and Proceedings of the Royal Society*, the *Journal of the Chemical Society*, and other publications, but several papers and laboratory notes by Drs. Turpin, Harden, Bailey, &c., now appear for the first time. Among these may be noted one "On New Forms of Stereometers," and another "On the Duration of Chemical Action in the Explosive Combination of Gases." The first part of the latter paper deals with the conduction of electricity by gases, and the author points out that, though we are far from having a clear mechanical theory on this subject, still some important advances towards the solution of the problem have recently been made.

E. Becquerel showed that air begins to conduct at a red heat, and that the conduction does not follow Ohm's law; again, Hittorf and others proved that mercury vapour at 360° does not conduct, an observation which is of special importance; while it is well known that air at the ordinary temperature and pressure is a perfect insulator. Dr. Turpin concludes that in gases the electrical conductivity is considerable only when molecular disruptions are proceeding in them, attended by the presence of free atoms; and following up this hypothesis, he attempts to measure the duration of the time of chemical action by measuring the time during which the gases will conduct electricity. The method herein described gave values of time, t, and resistance, R, connected with the explosive wave, but the real meaning of this time, t, was only perceived later on. The measurements of t only agree moderately, but as far as they go confirm the hypothesis put forward by Prof. Dixon, that in the explosion of the mixture H_2+O there is considerable dissociation in the wave-front, but that as one or other of the ingredients of the mixture is added in excess the dissociation diminishes.

The other papers cover a very wide range of subjects, both physical and chemical, and will doubtless be of interest to many readers.

The Manufacture of Alkalis and Acids. By Watson Smith, F.I.C., F.C.S. London.

The pamphlet now before us is an excerpt from Vol. xix. of the *Transactions of the Sanitary Institute*, being the report of a lecture given by Mr. Watson Smith on December 14, 1893. It may be briefly summarised as a short account of the acid and alkali manufactures from a hygienic point of view.

The author describes, with a fair amount of detail, the processes referred to above; but lays special stress on the dangers of leakage of the various gases and fumes generated in these manufactures, pointing out the proportion per cent, or per thousand, of these fumes which can be inhaled by human beings without causing death, as well as describing the principal symptoms engendered by the inhalation of some of the more deadly non-irritant gases. He shows that it is as much to the masters' interest, from a monetary point of view, as it is to the workmen, in their own protection, to prevent leakage of gases. He, moreover, states that in nearly every case of death by so-called "accidents" in modern works the "accident" has been caused almost entirely by the gross carelessness or wilful disobedience on the part of the sufferer. He concludes by giving a short list of the best antidotes and preventatives for the commoner kinds of mishaps.

The Universal Electrical Directory, 1894 (*J. A. Berly's*). London: Alabaster, Gatehouse, and Co.

The new edition of this Directory, being its thirteenth annual publication, has been thoroughly revised and enlarged by 104 pages. For simplicity and facility of reference it is divided into four groups, namely, British, Continental, American, and Colonial; these are again subdivided into alphabetical and classified sections. An improvement which we hope the editors will be able to adopt would be to make another section of the principal foreign towns, with a list of the electricians residing therein; this would undoubtedly be of great service, though it would probably entail a good deal of additional labour.

Besides the ordinary directorial matter, we are provided with an "up-to-date" table of the Electric Central Stations now in operation and in course of construction in Great Britain, wherein we find that there are at present no fewer than 83 stations actually working, besides some two dozen where the works are being constructed or about to be commenced.

Les Produits Chimiques Employés en Médicine. A. Trillat. Introduction par P. Schutzenberger. Paris: J. B. Baillière and Sons.

The science of chemistry and its applications have developed of late years to such an enormous degree that it becomes more and more difficult as time goes on for any one man to keep himself *au courant* with the new work which is continually being published. The natural outcome of this state of things is that men take up just one or two lines, and thus become, to a certain extent, specialists.

A book treating of all the diverse sections of modern chemical science would be unwieldy and beyond the competence of one man to produce.

The volume now before us is devoted entirely to chemicals employed in medicine and allied sciences, such as hygiene. It is addressed, however, not only to doctors and

pharmacists, but also to those engaged in, or wishing to familiarise themselves with, the manufacture of medicinal chemical products. The author has applied himself principally to the new synthetical methods, but has not ignored old processes which may have had recent improvements introduced. The first chapter is mostly historical. The second deals with antiseptics, and here we find a good many figures of various bacilli, shown multiplied 650 times; then follow several chapters devoted to the culture and destruction of these bacilli and the determination of antiseptic doses, the relations between chemical constitution and physiological properties, &c. The second section is divided into seven chapters, and describes the manufacture and properties of medical preparations derived from the fatty series, such as the ethers, chloroform, chloral, sulphonal, and their derivatives. The third, and last, section treats in a similar manner of those bodies useful in medicine derived from the aromatic series. Here we find several very interesting chapters on the distillation and rectification of tar from wood and oils, with descriptions of the latest forms of furnaces and stills used in their manufacture, and the methods employed in the preparation of the important group of disinfectants and their allies. A long chapter on the analytical character of the principal medical products, and the readiest methods of recognising them, completes the work.

There is a short list of *errata* which must not be overlooked; it is unfortunately placed in an inconspicuous position right at the end, and may easily be missed.

CORRESPONDENCE.

EXAMINATIONS.

To the Editor of the Chemical News.

SIR,—I am afraid Dr. Tilden did not carefully read my letter published in the CHEMICAL NEWS, vol. lxix., p. 72, as I made no allusion to the "position of chemistry at the Conjoint Board,"—whatever that may mean,—and most certainly expressed no opinion as to whether that "position" was satisfactory or unsatisfactory. My letter, which was written entirely from a teacher's point of view, directed attention to the present unsatisfactory system of examination adopted in this country, as applied to elementary pass examinations in science (theoretical), the case brought forward by Dr. Tilden in his first letter being a forcible example of the defects of that system.

His reply to my letter is, like the system he defends, unsatisfactory. He contents himself with saying that the examinations of the University of London and of the Science and Art Department are not as I described them. My statements were three—

1. That papers are set containing a limited number of questions.
2. That marks are assigned to the answers given.
3. That those candidates who obtain more than a certain proportion of the total marks are passed.

That 1 is as I state he cannot dispute. With regard to 2 and 3 I have made enquiries of examiners (past and present) appointed by the two examining bodies mentioned, and I find that these statements of mine are correct. Possibly this discrepancy arises from a misapprehension, and is my fault for not having explicitly stated that my remarks applied to elementary pass examinations; this I believed to be unnecessary.

That the system of examination is considered unsatisfactory by a large number both of teachers and of others who take an interest in scientific education is evident from the agitation which has been going on in London for some time past,—some advocating the reform of the University of London, others the establishment of a Teaching University,—the outcome being the appointment of a Royal Commission.

In some sciences—pure mathematics, for example—the system of written answers to set questions works more or less satisfactorily, because the facts are few and the processes many. In order to solve a mathematical problem successfully, the candidate must have had a mathematical training—he must have been *educated* in the subject. The same may be said of applied mathematics, for here, although more *facts* have to be learned by heart, they are far from being numerous, and it is easy for the examiner so to word the question as to make it not merely a test of the candidate's knowledge of the physical facts, but also of the mathematical process involved in solving the problem. In fact, in an examination in mathematics, whether pure or applied, there is comparatively little difficulty in ascertaining whether the student knows his mathematics or not.

In chemistry (elementary theoretical) it is quite another matter. The paper is set. Some candidates answer well; they get a certain percentage of marks; they are passed. Others, again, answer very badly; they get a low percentage of marks, and are rejected. Thus far the system, to some extent, serves its purpose. But how about the residuum—those who are neither very good nor very bad? How is the examiner to ascertain whether the candidate has really had a chemical education and profited by it, or whether he has simply "crammed" up a more or less incoherent mass of chemical facts? Dr. Tilden advocates that such cases should be disposed of according to their "merits," *i.e.*, I suppose, of the papers, but unfortunately he overlooks the fact that the merit of the paper and the candidate's knowledge of chemistry are not co-extensive. Ten minutes *viva voce*, or less, would settle the matter one way or another, but in examination by wholesale, as at the elementary Pass Science and Art Examinations or the London Matriculation, such a method is evidently impracticable.

Space does not allow me to enter into the important question of the degrading effect the incentive to "cramming" has had on chemical education.

In conclusion I may say I have read Dr. Ramsay's letter with great pleasure; there is scarcely anything in it with which I do not most heartily concur, and I think his idea of forming a Committee of Teachers with the object of reforming the present examinational system an admirable one.—I am, &c.,

CHARLES E. GROVES.

Guy's Hospital, London,
February 24, 1894.

EXAMINATIONS.

To the Editor of the Chemical News.

SIR,—Professor Tilden says that the Science and Art Examinations are not conducted in the way Mr. Groves describes. Will he be so good as to dispose of the following question according to its merits, and inform us what became of the candidates who failed to answer it?

"Science and Art Department, 1891.—Subject X., No 63.

"Six grms. of magnesium sulphate are dissolved in 100 grms. of water; the observed depression of the freezing-point is 0·958°. Taking the value of T as 37, what formula most probably represents the state of the dissolved salt?"

The answer given in Thorpe's "Chemical Problems," and apparently thus sanctioned by the other examiners, is $Mg.SO_4.7H_2O$.

How can this be shown? Perhaps it is as well that a rigid system of marks is not in use at South Kensington.—I am, &c.,

X, Y, AND Z.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 7, February 12, 1894.

Aimé Girard has been elected a member of the Academy (section of Rural Economy) *vice* Chambrelent, deceased. The unsuccessful candidates were Laboulbène and Müntz.

New Experiments on the Reproduction of the Diamond.—Henri Moissan.—In the different conditions in which the author has experimented he has been able to obtain a variety of carbon, black or transparent, certain specimens of which presented a well-marked crystalline appearance. Their specific gravity was comprised between 3 and 3·5. They scratched ruby. They resisted twelve times the action of a mixture of dry potassium chlorate and fuming nitric acid. They burnt in oxygen at a temperature bordering on 900°, yielding four times their weight of carbonic anhydride.

Fusibility of Isomorphous Saline Mixtures.—H. Le Chatelier.—The author has undertaken to study the crystallisation temperatures of isomorphous saline mixtures. He calls those substances isomorphous which, whatever their chemical composition, crystallise together in proportions varying in a continuous manner.

Assimilation of Gaseous Atmospheric Nitrogen by Microbia.—S. Winogradsky.—In summing up the chemical character of the fixation of gaseous nitrogen, the author holds that the phenomenon seems to be an effect of the meeting of gaseous nitrogen and nascent hydrogen in the midst of living protoplasm.

Zeitschrift fur Analytische Chemie.
Vol. xxxii., Part 5.

Borax as a Basis for Alkalimetry.— Th. Salzer.—Already inserted.

Determination of Phosphorus in Siliciferous Steel and in Crude Irons.—J. Spüller and S. Kallman.

Proportion of Fluorine in Teeth.—Dr. E. Wrampelmeyer.—Already inserted.

A New Gas Volumeter of Universal Applicability.—F. Gantter.—This paper requires plate IV.

Analysis of Silicon Carbide.—Dr. Otto Mühlhaeuser.—Already inserted.

Determination of Nicotine in Tobacco. — Dr. Richard Kissling. — The author defends his process against the criticisms of Dr. Vedrödi.

Determination of Cyanogen in Spent Gas Purifying Masses.—Dr. W. Leybold.—A reply to Knublauch and Drehschmidt.

Line Spectra of Certain Elements.—H. Kayser and C. Runge (*Chemiker Zeitung*).—The authors have examined the spectra of aluminium, indium, and thallium, and the ultra-red spectra of the alkalis.

Absorption-spectra of the Metals.—W. L. Dudley.—From the *American Chemical Journal.*

Contributions to Quantitative Spectroscopic Analysis.—G. and H. Krüss (*Zeitsch. fur Anorg. Chemie*).—A comparison of different methods, and an account of the influence of temperature upon the absorption-spectra of coloured solutions.

Combination of the Examination in the Dry and the Wet way.—W. E. Adeney and T. A. Shegog.—From the CHEMICAL NEWS.

Separation of Different Mineral Species.—J. W. Retgers (*Recueil des Travaux Chimiques des Pays-Bas*).—The separation depends on the behaviour of the groups of minerals in question on introduction into solutions and fused saline masses of different specific gravities. The author removes quartz by immersion in Thoulet's solution (mercuric iodide and potassium iodide in water) of specific gravity 2·7. The residue which sinks in this solution is separated by means of a heavier Thoulet's solution (specific gravity 3·0) or by solutions of iodine in methylene and xylene, which separate the minerals free from iron from those containing iron. The latter are treated with a solution of iodine in methylene alone (specific gravity 3·3). The supernatant amphibole is removed, and the further separation (the pyroxene group) effected by means of barium mercuric iodide or the author's mixture of iodine and iodoform in methylene iodide (3·60 to 3·65). The residue which did not float consisted of garnets and small quantities of rutile, zircon, and iron ores. To separate these, Retgers used a watered melt. From 1 kilo. of sand the lighter minerals were first removed with Thoulet's solution (3·0 to 3·2). Then followed a separation with thallium silver nitrate heated to 70°—75° and reduced with water to specific gravity 4·2. Augite, hornblende, and garnet were thus removed. By concentrating the melt to 4·5 the author separated rutile, whilst from the residue (zircon and iron ore) the latter was removed by means of the magnet.

Intermixture of Two Liquids with Exclusion of Air.—L. Kentmann (*Pharm. Centralhalle*).—The author uses a 3-necked Woulf's bottle, the necks of which are closed with stoppers simply perforated. Through one neck is introduced a gas-delivery pipe, by means of which, after pouring one of the liquids into the bottle, any desired gas can be introduced and the air expelled. The second neck is fitted with a Bunsen caoutchouc valve opening outwards, and therefore permitting the exit of air, but not its entrance. To the third neck is fixed a burette with a glass cock, filled with the second liquid. To protect this from the action of air, and to hinder the entrance of air into the mixing-bottle, liquid paraffin is poured upon the liquid so as fill the burette entirely. In order to allow the entrance of the second liquid, the upper end of the burette is connected with a gas-generating apparatus.

MISCELLANEOUS.

Electro-Chemical Company, Lim.—Letters of allotment were posted on Tuesday, February 27.

Fletcher's Autometric Stopper.—We have received a sample of this ingenious contrivance, and have found it to work in an exceedingly satisfactory manner. As its name indicates, it is a combined bottle-stopper and measuring tube, the latter being graduated either in *minims* or *cubic centimetres*. By loosening the stopper, which is made of indiarubber, and slightly compressing the air-chamber attached, any required volume of liquid can be instantly withdrawn from the bottle, and by pressing an ingenious valve on the top very minute quantities of the liquid can be expelled for making accurate measurements. These stoppers and bottles are at present made in four sizes, to measure 30, 60, and 120 minims, and 5 c.c.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Liquid Chlorine.—I think your correspondent could obtain a supply of liquid chlorine from the Rhenania Chemical Works at Aix. If, however, he only requires a small quantity, I could probably myself present it to him if he will send me his name and address.—W. A. SHENSTONE, Clifton College, Bristol.

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Society of Arts, 8. (Cantor Lectures). "The Decorative Treatment of Artificial Foliage," by Hugh Stannus, F.R.I.B.A.
—— Society of Chemical Industry, 8. "The *Zymæan* Metallurgy," by Admiral J. H. Selwyn. "The Commercial Production of Chlorine by the Ammonia-Soda Process," by F. Bale. "Notes on Lithographic Varnish," by F. H. Leeds, F.I.C.
—— Medical, 8. (General Meeting).
TUESDAY, 6th.—Royal Institution, 3. "Locomotion and Fixation in Plants and Animals," by Prof. Charles Stewart, Pres.L.S.
—— Institute of Civil Engineers, 8.
—— Pathological, 8.30.
—— Society of Arts, 8. "Travels in the Basin of the *Zambesi*," by Mons. Foa.
WEDNESDAY, 7th.—Society of Arts, 8. "Refrigerating Apparatus," by Prof. Carl Linde.
—— Geological, 8.
THURSDAY, 8th.—Royal, 4.30.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
—— Medical, 7. (Annual Dinner).
—— Royal Institution, 3. "The Vendânta Philosophy," by Prof. Max Müller, M.A.
—— Society of Arts, 4.30. "The Indian Currency," by J. Barr Robertson.
FRIDAY, 9th.—Royal Institution, 9. "The Making of a Modern Fleet," by William H. White, C.B., F.R.S.
—— Astronomical, 8.
—— Physical, 5. "Calculating Machines, and especially a New Harmonic Analyser," by Prof. O. Henrici, F.R.S.
SATURDAY, 10th.—Royal Institution, 3. "Light, with special reference to the Optical Discoveries of Newton," by the Right Hon. Lord Rayleigh, F.R.S.

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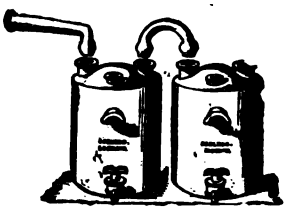

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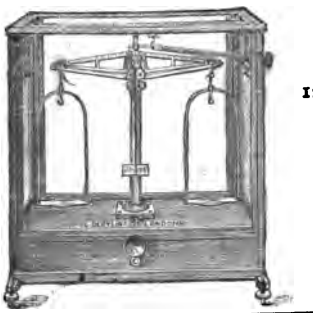

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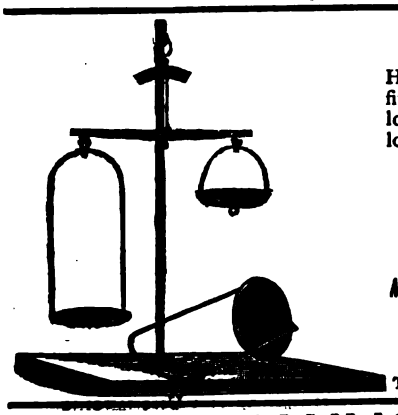

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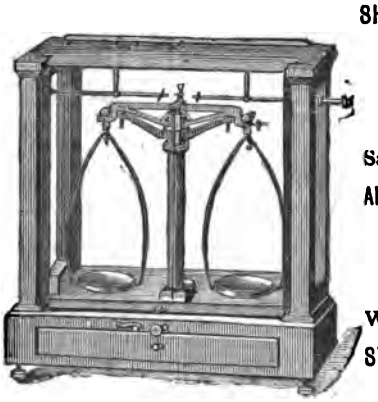

FIG. 3a.

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THE CHEMICAL NEWS.

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THE ACTION OF HEAT UPON ETHYLENE.*

By VIVIAN B. LEWES.

(Continued from p. 103).

In a paper read before the Chemical Society (*Journ. Chem. Soc.*, lxi., p. 322) I showed that in the interior of a luminous flame the olefines are to a great extent converted into acetylene, which decomposes at about 1200° C. with liberation of carbon, which being heated partly by its own combustion and partly by the combustion of methane and hydrogen, becomes incandescent, and gives luminosity to the flame, and in the experiments which I have described I fully expected to find a higher percentage of acetylene; but the great tendency towards polymerisation which that body exhibits seems to at once determine its conversion into benzene, which can readily be distinguished among the liquid products, whilst a number of other more complex hydrocarbons are produced, among which crystals of naphthalene are conspicuous.

In order to ascertain if the behaviour of acetylene when passed through the heated tube under the conditions of these experiments gave results which support this view, acetylene was prepared by the action of dilute hydrochloric acid on acetylide of copper.

Analysis of Original Gas.

Acetylene	94·28
Oxygen	1·12
Nitrogen	4·60

The gas was passed through the platinum tube, 25 m.m. of which was heated to a temperature of 1000° C.

Analysis of the Heated Gas.

Acetylene	25·95
Other unsaturated hydrocarbons	61·97
Saturated hydrocarbons	3·21
Carbon monoxide	1·01
Oxygen	0·38
Hydrogen	1·50
Nitrogen	5·98
	100·00

Carbon and Oil formed per 100 c.c. of Gas.

Oil	0·095
Carbon	0·018
Volume before heating ..	309 c.c.
„ after „ ..	174·2 c.c.

showing that even under these conditions nearly three-quarters of the acetylene had undergone polymerisation; so that it is probable that in the case of nascent acetylene, liberated from ethylene by the action of heat, the condensation of the acetylene molecules to form benzene would be practically instantaneous, unless the temperature were sufficiently high to cause dissociation to carbon and hydrogen at the moment of liberation.

The unsaturated hydrocarbons consisted chiefly of ethylene with some benzene vapour, the ethylene probably having been formed by the direct combination of acetylene and hydrogen, an interaction first noticed by Berthelot—

$$C_2H_2+H_2 = C_2H_4.$$

This also accounts for the small quantity of free hydrogen found on analysis, which, having regard to the amount of carbon deposited, should have been considerably higher.

It will be noticed that with the rate of flow employed in the experiments shown in Table I., the largest amount of acetylene found in the gas after heating was 3·60, which occurs just at the temperature when carbon begins to deposit freely, and is therefore sufficiently high to check the polymerisation of the acetylene, and many attempts were made to find conditions under which the acetylene could be liberated and prevented from polymerising, and it was found that this could apparently be, to a certain extent, effected either by diluting the ethylene with a considerable volume of an inert gas, or else increasing the rate of flow through the heated tube.

On heating a mixture of 75 per cent hydrogen and 25 per cent ethylene through the tube, heated as before, 3·43 per cent of acetylene was produced, which would be equivalent to 13·72 on the ethylene present, whilst the following results show the effect of increasing the rate of flow of the gas through the tube. The original gas taken was a bad sample containing 87·49 per cent of ethylene and 12·51 of nitrogen, and the rate of flow was increased to 15 c.c. per minute, the tube being heated to 1250° C.

Unsaturated hydrocarbons	10·41
„ „ containing acetylene	4·49
Saturated hydrocarbons	34·00
Hydrogen	41·99
Nitrogen	9·11
	100·00
Increase in volume	Large
Carbon and oil deposited	0·006 grm. per 100 c.c.

showing a very marked increase in the amount of acetylene formed.

Before it was possible to trace the primary action taking place during the heating of ethylene, it was necessary to find how the temperatures and methods I was employing affected pure methane, which plays so important a part amongst the products of decomposition.

Methane was prepared by acting on methyl iodide by means of the copper zinc couple in the presence of alcohol and water.

TABLE IV.—*The Action of Heat upon Flowing Methane.*

Percentage of methane in the original gas ..	99·2	99·2	99·2	99·2
Temperature of gas in the decomposing tube	1000° C.	1200° C.	1300° C.	1500° C.
Analysis of the gas after heating—				
Unsaturated hydrocarbons	trace	0·07	0·39	1·20
Containing acetylene	trace	0·07	0·39	0·963
Saturated hydrocarbons	97·65	90·00	88·52	19·22
Hydrogen	1·55	8·53	10·37	78·66
Carbon deposited and oil formed in grms. per 100 c.c. of gas—				
Carbon	0·0	0·0	trace	0·015
Oil	0·0023	0·0025	0·0005	0·0

These results show how much more stable methane is under the influence of heat than any of the other gaseous hydrocarbons studied.

It probably decomposes at first into acetylene and hydrogen, according to the equation—

$$2CH_4 = C_2H_2+3H_2,$$

and then the acetylene either polymerises or decomposes to carbon and hydrogen, according to the temperature.

These results also explain why it is that the flame of methane when burning at an open tube is practically non-

* A Paper read before the Royal Society.

luminous, as, under these conditions, the maximum temperature of the flame is below 1100° C., and no formation of acetylene takes place; whilst with increase of temperature the flame becomes rapidly more and more luminous, so that when burnt in a regenerative burner at 1500° C. the light emitted is of considerable illuminating value.

(To be continued.)

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

SECOND PAPER: THE ANALYSIS OF BARIC CHLORIDE.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 103.)

Ratio of the Chlorides of Silver and Barium.

THE properties of the two chlorides having been studied as far as they are concerned in the present work, it was now possible to compare their molecular weights. Very definite advice with regard to the precautions necessary in such a comparison has been given by Stas (*Mem. de l'Acad. Belg.*, xliii., Part ii., p. 66), and most of his suggestions have been found of use. One recommendation, however, although most useful for ordinary work, is of questionable propriety when applied to the most precise work. In order to prevent argentic chloride from being dissolved by the water used for washing it, Stas advises the exclusive use of a very dilute solution of argentic nitrate for the purpose. (Professor Cooke also suggested this method of procedure, *Proc. Amer. Acad. Arts and Sciences*, xvii., 7). I have found it very difficult wholly to free argentic chloride from traces of the nitrate, even by long-continued shaking with pure water, and of course this difficulty is increased by the presence of additional impurity. The small amount of argentic nitrate which is certain to be left behind, according to the method of Stas, decomposes and blackens a little of the chloride upon fusion, even in the dark; and no suitable correction can be applied to counteract the error. Accordingly, pure water was always used for the final washings during the present work. These wash-waters were all evaporated, and the small amount of argentic chloride present was determined in the manner which has already been described. It is thus tolerably certain that the necessary errors of the analytical process did not exceed the tenth of a m.grm.

In two preliminary experiments very pure baric chloride was ignited at a dull red heat to constant weight, dissolved in water, and corrected for the amount of alkali found. It was then precipitated, when perfectly cool, by pouring it into a slight excess of silver dissolved in nitric acid, and diluted with about forty times its weight of cold water. The precipitate was very thoroughly shaken for several days, and washed by decantation until the wash-water was no longer acid. It was then transferred with great care to a Gooch perforated crucible, washed for some time longer, dried at 180°, and weighed. Both of the precipitates were slightly coloured, and each lost about 1-10,000th of its weight upon fusion in a covered porcelain crucible. In calculating the results it was necessary to subtract the amount of argentic chloride equivalent to the small *excess* of hydrochloric acid usually added in determining the amount of alkali formed by the ignition, as well as to add the amount of argentic chloride found in the wash-water. The corrected results are given below, the details having been omitted; but the particulars will be given with regard to all the important determinations.

Preliminary Determinations.

$2AgCl : BaCl_2$.

No. of expt.	Corrected weight of baric chloride.	Corrected weight of fused argentic chloride.	100,000 parts of argentic chloride correspond to *n* parts baric chloride.	Atomic weight of barium.
	Grms. in vacuum.	Grms. in vacuum.	*n* =	
18.	6·7295	9·2637	72·644	137·411
19.	5·4597	7·5161	72·640	137·400
		Average		137·406

Since the experiments were carried on in the dark, the purplish colour of the fused argentic chloride indicated that argentic nitrate had been occluded, in spite of the considerable care used in washing the precipitate. In order to determine whether this occlusion had been due to the concentration of the silver solution, an experiment was made by pouring a solution of a definite amount of pure baric chloride into a very strong solution of argentic nitrate. 2·6088 grms. (corrected) of baric chloride yielded 3·5929 grms. (corrected) of carefully washed argentic chloride. The ratio deduced from these figures is $2AgCl : BaCl_2 = 100 : 72·609$, a result almost 1-2000th lower than the last; and the consequent value of the atomic weight of barium is only 137·31. The argentic chloride was of a very deep purple colour.

The outcome of these experiments showed the necessity of Stas's usual practice of having the silver solution very dilute; in the subsequent work the dilution was usually 1 : 100, and sometimes even greater.* Moreover, the nitrate was always in future poured gradually into the baric chloride, so that until the very last an excess of chlorine should be present in the solution.

In the first series of the final group of experiments the baric chloride was ignited at a dull red heat in air or nitrogen; in the second series the salt was ignited and fused at a bright red heat in a stream of pure hydrochloric acid; and in the third it was not ignited at all. The simplest manner of explaining the method of procedure adopted in the three series of analyses which follow is to give the detail of one of the experiments.

(To be continued).

THE SEPARATION OF COBALT AND NICKEL.†

By H HERRENSCHMIDT and E. CAPELLE.

THE authors have re-examined the potassium nitrite and the potassium cyanide method of Liebig. With potassium nitrite they were not able to effect a complete separation of the two metals, since nickel could be found in the cobalt and cobalt in the nickel. The potassium cyanide method, performed exactly in accordance with the directions of R. Fresenius, gave, indeed, better results, but still left something to be desired. In the closer examination of this method the authors used the microscope. They observed that chemically pure cobalt hydroxide is not black, as asserted by various authors, but has a light brown colour, whilst nickel hydroxide has a pure black colour. On a microscopic scrutiny of the recently precipitated hydroxides, cobalt hydroxide has always a light brown and nickel hydroxide a black colour. A cobalt hydroxide containing only 1 per cent of nickel shows under the microscope an almost purely black field. Hence nickel may be detected microscopically in cobalt solutions in which the usual reactions no longer indicate

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*,

* In some cases Stas used only 15 to 30 c.c. of water for every grm. of silver, in spite of his good advice to the contrary (*Mem. Belg.*, &c. xliii., Part 2, p. 11).

† *Zeitschrift Analytische Chemie.*

a trace of nickel; the recently precipitated hydroxides display black points among very numerous brown points. The presence of iron and manganese does not prevent the recognition of nickel.

In order to test a solution of cobalt in this manner for traces of nickel, it is almost completely neutralised with potassa or soda-lye, and sodium hypochlorite is then added in slight excess. Several portions of the precipitate are then taken and examined microscopically with magnifying powers of from 180 to 200 diameters.

For detecting a little cobalt along with much nickel, Herrenschmidt and Capelle utilise the well-known fact that nickel hydroxide suspended in a neutral or an alkaline liquid passes completely into solution in the cold and in a gentle heat (50°) if a current of chlorine is passed into the liquid. Cobalt hydroxide remains undissolved under the same conditions.

In order to test for cobalt in the nickel hydroxide separated by the potassium cyanide method, the washed precipitate is suspended in water, and a current of chlorine free from hydrochloric acid is passed into the liquid. Here a greater or less proportion of the precipitate remains undissolved. It is filtered off, and on examination with a borax bead it will be found to be cobalt, and on further microscopic scrutiny to be free from nickel.

The use of these two methods of examination led the authors to the result that for the separation of cobalt and nickel the potassium cyanide method is preferable to that with potassium nitrite. In determining cobalt and nickel in ores, oxides, &c., they proceed as follows:—

After precipitation with sulphuretted hydrogen in a hydrochloric solution, and after repeated elimination of iron and alumina with ammonium carbonate, the liquid is precipitated with ammonium sulphide in slight excess, and the mixture is allowed to stand for some minutes. Acetic acid is then added in slight excess, and the liquid is heated to ebullition. The precipitate obtained is rapidly filtered, and washed with a boiling solution of ammonium acetate. The precipitate is dissolved in nitric acid, the solution evaporated to dryness, again taken up with water, and the residue, after filtering off the undissolved sulphur, is brought to a known volume. One half of the solution is evaporated to dryness in a weighed platinum capsule, the residue moistened with some drops of sulphuric acid, heated at very faint redness until the weight is constant. The weight gives the sum of the cobalt and nickel sulphates, with which is mixed, in the state of sulphate, any zinc which may be present.

The second half of the solution is precipitated with potassium cyanide and bromine exactly as directed by R. Fresenius. The precipitate of nickel hydroxide, well washed, is treated with chlorine in the manner mentioned above, and the small portion of cobalt hydroxide remaining undissolved is filtered off. The latter is further examined as already described. The solution of nickel is slightly acidulated with hydrochloric acid, and after the chlorine is expelled by boiling it is poured into boiling soda-lye. The hydrated nickelous oxide obtained is filtered thoroughly, washed, and again dissolved in hydrochloric acid. The solution is evaporated to dryness in a weighed platinum capsule, the residue is moistened with sulphuric acid, and the nickel is obtained as sulphate by heating to very faint redness. The quantity of cobalt present is found from the difference.

If zinc is present the weighed sulphates from the first half of the solution are re-dissolved, the solution is mixed with ammonium acetate and acetic acid, and the metals are precipitated with sulphuretted hydrogen. The sulphides obtained are treated with very dilute sulphuretted hydrogen. The solution is neutralised, mixed with potassium cyanide, and the zinc precipitated with potassium sulphide. The weighed zinc sulphide is calculated as sulphate, and deducted from the sum of the sulphates.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 15th, 1894.

Dr. Armstrong, President, in the Chair.

Certificates were read for the first time in favour of Messrs. Samuel Bernard Asher-Aron, P.O. Box 1021, Johannesburg; Joseph Beynon Ashcroft, 96, Warner Street, Derby; Oswald Ernest W. Hewitt, 116, Burnt Ash Hill, Lee, S.E.; Charles T. W. Hirsch, Fiji Islands; Edwin James Jackman, 152, Upton Lane, Forest Gate, E.; Alexander Mitchell Kellas, 24, Cecil Park, Crouch Hill, N.; John Abraham Kelly, Hyderabad, Deccan; Thomas John Roberts, 31, North Road, St. Helens, Lancashire.

The following were elected Fellows of the Society:—William Edward Bamber, William Rowland Bird, Chuni Lal Bose, William Good Boul, M.A., Herbert Edward Burgess, John Cannell Cain, F. D. Chattaway, Herbert Henry Dains, Samuel Henry Davies, Dr. John Duncan, Basil Leonard Dunne, Frank Evershed, Joseph Addey Fawcett, Henry Purefoy Fitzgerald, Walter Grafton, Robert Hamilton, Edward Frank Harrison, W. Pellew Harvey, Edward Stanley Haward, Edmond Herbert Hills, John Winder Holmes, R. Hornby, B.A., Frank Hughes, Alfred Hutchinson, David Hamilton Jackson, M.A., B.Sc., Walter Jardine, George F. Jaubert, Ph.D., Francis Herbert Jennison, Robert Leonard Jenks, A. Lapworth, Clifford Walker Lee, Norman Leonard, E. W. Lucas, Arthur Luty, A. H. Macdonald, Godfrey Melland, J. M. Murray, B.Sc., David Paterson, Richard Paulusz, William Henry Pearson, John Peden, jun., J. Holmes Pollok, J. Cardwell Quinn, A. B. Robertson, Arthur Ross, Richard A. Rouillard, Walter Smithson Rowntree, Charles Henry Smith, Alfred E. Tanner, George Trench, William Lloyd Williams, Hamilton More Wingate, B.Sc., Meredith Young, M.B., C.M. (Edin.).

It was announced that the following changes in the Council List were proposed by the Council:—

As *Vice-Presidents*—Mr. Horace T. Brown and Mr. Ludwig Mond *vice* Mr. J. Pattinson and Professor Tilden.

As *Members of Council*—Mr. A. G. Green, Dr. Kipping, Dr. Stevenson, and Professor Sydney Young, *vice* Dr. Collie, Mr. L. Fletcher, Mr. M. M. P. Muir, and Mr. F. J. M. Page.

Mr. E. J. Bevan, Dr. Lawson, and Mr. E. W. Voelcker were appointed by the meeting to audit the Treasurer's accounts.

Of the following papers that marked * was read:—

*114. "*The Analytical Determination of probably Available 'Mineral' Plant Food in Soils.*" By Bernard Dyer, D.Sc.

The paper contains a short notice of the principal papers hitherto published on this subject, and an account of a series of preliminary experiments made by the author in endeavouring to decide what was the most useful solvent for extracting "available" (as distinguished from "total") mineral constituents of plant food from soil.

These experiments led him to seek to determine the average acidity of the root sap which plants have at their disposal as a natural solvent for such constituents. Determinations involved in the examination of about 100 plants, made in order to arrive at this, are recorded in detail.

As these determinations appeared to indicate the suitability as an analytical soil-solvent of a 1 per cent solution of citric acid—the same solution that, on grounds quite differently approached, had been suggested by Tollens and Stutzer as an agent for like purposes in testing manures—the authors decided to try the effect of the solution on soils of known history and recorded fertility.

For the purposes of this trial, twenty-two separate plots of the experimental barley field at Rothamsted were sampled, with the kind permission and assistance of Sir John Lawes and Sir J. Henry Gilbert, and the samples were all subjected to separate investigation. A detailed account of this work is given, and its results discussed, the general conclusion being that the use of the suggested solution does give valuable indications of comparative ("mineral") soil fertility such as are not obtained in ordinary soil analysis.

Appended to the account of the work on soils is an account of some experiments on phosphatic manurial materials, comparing the solvent action of alkaline ammonium citrate and dilute citric acid, the result of which is to confirm the views of Tollens and Stutzer, to the effect that, although ammonium citrate may suffice to dissolve "reverted" or "retrograde" phosphate, it does not suffice to indicate "available" phosphate, and that its use ought to be superseded by that of a weak solution of citric acid.

Discussion.

Sir Henry Gilbert thought all would agree that Dr. Bernard Dyer had entered on a very interesting and very useful line of enquiry. It might be of interest if he referred a little more to the history and difficulties of soil analysis, and if he called attention, in more detail than Dr. Dyer had done, to the chemical statistics of the crops, and to the amounts of the crops themselves, in the case of some of the plots to which Dr. Dyer's results related. At the time of the commencement of the Rothamsted investigations, now more than fifty years ago, the assumption was, that the analysis of the soil, and of the ashes of the crops to be grown, supplied the essential data upon which to found an opinion as to the manurial requirements of the soil. They soon came to the conclusion however, that such a view was fallacious; and they were somewhat sharply called to account by scientific friends for not adopting such obvious and fully authorised means to a desired end. The discussions at that date as to the nitrogen in soils afforded a good illustration of the difficulty in regard to other constituents also. The contention that the application of nitrogenous manures for the growth of crops was unnecessary was fortified by the results of the determinations of nitrogen in twenty-two different soils by Dr. Krocker; and it was further confirmed by results obtained on fourteen different soils, each analysed by three different chemists, for the Landes-Oekonomie Kollegium at Berlin, under the direction of Professor Magnus. It was calculated that these different soils contained amounts of nitrogen, reckoned as ammonia (though of course they did not exist as such), varying from 3000 to 18,000 lbs. per acre. In reference to these amounts and the argument founded on them, Sir John Lawes and he had pointed out that if 100 lbs. of nitrogen in the form of ammonium salts were applied to an acre of soil weighing 4,000,000 lbs., it would only raise the percentage in the soil by 0·0025, or by 1 in 40,000, and yet that in many cases such an addition would give an enormous increase of crop, although the soil might contain thousands of pounds of combined nitrogen. It happened, however, that there were very great discrepancies between the determinations, not only of nitrogen, but of other constituents, in the same soil by the three different analysts; and Professor Magnus himself concluded, in regard to the series, that in the existing state of science little was to be expected from the analysis of soils; Sir John and he also argued that little advance could be looked for without special investigation and adaptation of methods of analysis to the requirements of the subject.

In 1863, that is a few years after the establishment of Agricultural Experiment Stations in Germany, a Commission of Agricultural Chemists was appointed to consider the question, and settle on a uniform method of soil analysis, so that the results obtained by different analysts might be comparable. In 1864 Professor E. Wolff reported the conclusions of the Commission; and, so far as solvents were concerned, concentrated cold, and concentrated hot, hydrochloric acids were adopted, though Wolff at the same time suggested that it would be well to use pure water also. Peters, however, proposed that carbonic acid water and dilute acetic acid should also be used. The subject was, he thought, further investigated, but whether or not the suggestion of Peters was finally adopted he did not remember. However, some years later, Hermann von Liebig having asked for samples of some of the plots of the Rothamsted experimental wheat field, samples from five plots, to three depths of 9 in. each, in each case, were supplied to him; and he determined in them, besides other constituents, the potash and the phosphoric acid, the former in a dilute acetic acid extract, and the latter in a dilute nitric acid extract. These results unmistakably showed differences in the amounts of potash and phosphoric acid in the soils according to the manures employed; and they further brought out the interesting fact that comparatively very little of the applied potash or phosphoric acid had gone below the first 9 in. of soil, and that certainly none had gone into the third depth. This is consistent with the fact that, in a series of complete mineral analyses of the drainage waters from the plots made by the late Dr. Voelcker, only very small amounts of either potash or phosphoric acid were found in them.

Lastly, some years later still, Dr. Carl Schmidt, of Dorpat, made a considerable series of analyses of various soils, in which he used 1 per cent and 5 per cent hydrochloric acid cold, and 10 per cent hot, and, lastly, acid, alkali, and fluoric acid; and, of course, the results showed very different amounts of the various constituents according to the solvent used.

Such was the position of the question when he found himself compelled to treat of it in his Oxford lectures about ten years ago. The course adopted was to bring forward published analyses of very various descriptions of soil; then, after excluding all other constituents, to bring together at one view the actual and comparative amounts of the potash and phosphoric acid only, and to the results as so presented he endeavoured to give some interpretation by reference to the results of Hermann von Liebig and Professor Carl Schmidt.

More recently, two well-known agricultural chemists in Germany (Professor Hellriegel and Professor Maercker) finding that, in their capacity of consulting chemists in their respective districts, the analysis of soils as conducted in the ordinary way afforded them little or no guidance as to the advice to be given for their manuring, each instituted an extensive series of vegetation experiments in pots, with a view to the elucidation of the subject. He was not aware, said Sir Henry Gilbert, that either had as yet published his results and conclusions in reference to the point in question. It was of much interest to observe, however, that it was in the course of these experiments, instituted with a totally different object, that Hellriegel first observed nodules on the roots of some of his leguminous plants, and, coincident, greatly increased luxuriance of growth. Thus, it is to the difficulties of soil-analysis, and the proper interpretation of the results, that we owe Hellriegel's investigations on the fixation of free nitrogen. As to Professor Maercker's experiments, he was not able to give an accurate account of their plan; but he was kind enough to show the speaker his large series of pots under experiment in 1891; and, so far as he remembered, his scheme, stated in a few words, was somewhat as follows:—Four characteristic soils of the neighbourhood were taken for experiment, and these were examined by the aid of different solvents, and he believed dilute citric acid was one; and then a great variety of plants, representing, therefore, very various collective capacities, were grown. If, for example, the available condition of the potash in the various soils, for the various descriptions of plant, was the question, care was taken that other constituents than potash should not be wanting,

and the plants were grown either without or with known additions of potash. If phosphoric acid was the point of enquiry, a similar plan, *mutatis mutandis*, was adopted. Eventually the potash or the phosphoric acid, as the case might be, was to be determined by solvents of various strengths, with a view to founding, on the results, a system of examination of soils such as would indicate their requirement or otherwise for different manures.

With reference to the chemical history of the crops of a few of the plots, the potash and phosphoric acid results relating to which Dr. Dyer had given in his paper:—The barley plots, in relation to the crops of which we have the most complete analytical data, are Nos. 2*a* and 4*a*. Each of these has received, during forty years in succession, an amount of ammonium salts supplying 43 lbs. of nitrogen per acre per annum. Each has also annually received superphosphate. 2*a* has received no potash from the beginning, but 4*a* has received potash, soda, and magnesia salts every year. They had complete analyses of the ashes of the grain and of the straw of each of these plots, representing respectively periods of ten, ten, ten, and ten years, or, in all, the forty years to 1891 inclusive. The table exhibited showed that whilst over the first ten years the crop without potash supply yielded 35·6 lbs. of potash per acre per annum, the amount went down in the succeeding decades to 30·9, 19·5, and 15·7 lbs. per acre per annum. Against these amounts, the crops grown with an annual supply of potash showed the following quantities per acre per annum over the successive decades, 53·7, 63·7, 51·5, and 44·8; or, over the whole period of forty years, the potash-exhausted plot gave 25·4 lbs. of potash per acre per annum in the crops, whilst the crops on the plot with the potash supply gave an average of 53·4 lbs., or more than twice as much. The details further showed that the decline from period to period without supply was, in the grain, proportionally much less than that in the straw; the result, apparently, being that, provided the climatic conditions were favourable, matured grain might be formed almost to the exhaustion of the migratory potash of the rest of the plant, as indicated by the small amount retained in the straw. It was remarkable that with these very great differences in the amounts of potash taken up, in the one case without, and in the other with, an annual supply of it, there was, over the forty years, not quite one bushel of grain per acre per annum less yielded on the plot without supply than on that with it. Over the last ten years, however, the yield of grain without supply of potash had gone down very much, and that of straw had been less without supply than with it over each of the ten-yearly periods, and considerably so over the last two decades, and especially in the last. In fact the total growth had become gradually less, and the susceptibility to adverse seasons had been more and more marked in the later years.

The table of Dr. Dyer's results with the entire series of plots, showed at a glance the comparative exhaustion or accumulation of both potash and phosphoric acid, whether hydrochloric acid or a 1 per cent solution of citric acid was used. But confining attention to the two plots 2*a* and 4*a*, of the crops of which they knew more of the chemical history, it would appear that whilst not more than two-thirds of the potash estimated to be accumulated where it was supplied was taken up even by hydrochloric acid, approximately the whole of the accumulated phosphoric acid was so taken up. Hence it may be judged that much of the residue of the supplied potash must have gone into more fixed combinations within the soil than was the case with the phosphoric acid. Then as to the citric acid results, it was to be observed that they are so far accordant, that the sample of the potash-exhausted plot taken in 1882 showed more potash than that taken in 1889, when the exhaustion was greater; and, again, the citric acid determinations on the soil with potash supply showed more so taken up from the 1889 than from the 1882 sample, the accumulation having, of course, been the greater at the later date. It was further of interest to observe that the amounts determined in the potash-exhausted soil by the citric acid solution were about from three to five times as much as the crops annually took up, which is a fairly consistent relation. Lastly, with reference to these barley soil results, as superphosphate was applied to both plots, the comparison of the amounts taken up on the two was of less interest than in the case of the potash. These two plots, in fact, are of special interest as illustrating in the one case actual exhaustion, and in the other actual accumulation of potash; there being in the one case a loss over the forty years of about 1018 lbs. of the potash of the soil, and in the other a gain from supply of about 3180 lbs.

But Dr. Dyer was also working on the soils of some of the plots of the experimental wheat-field, and these would afford some striking illustrations of the effect of accumulated residue of potash supply over a long series of years. Thus, there are four plots, 11, 12, 13, and 14, each of which during the forty years to 1891 inclusive, received ammonium salts = 86 lbs. nitrogen per acre per annum, and also superphosphate each year. Plot 11 had received no potash either during those forty years or during the eight preceding years of the experiments. Plot 12 received 587 lbs. of potash during the first eight years, but none during the succeeding forty years, but it received a soda-salt instead; Plot 13 received about 737 lbs. of potash during the first eight years, and also a liberal supply of potash in each of the succeeding forty years; lastly, Plot 14 received 566 lbs. of potash during the first eight years, but none since; but a magnesia salt instead. Thus, Plot 11 had received no potash throughout the forty-eight years; Plot 12 had received none during the last forty years, but there would be a residue from the applications during the preceding eight years; Plot 13 had received potash every year; and Plot 14 no potash during the forty years; but it would have a residue from the previous applications. We had, therefore, in the comparison of the results obtained on Plots 12 and 14 with only residues of potash from long previous applications, with those on Plot 11 without any potash supply at all, and on Plot 13 with an annual supply of it, the means of judging whether the residue of potash from the applications during the first eight years had been effective. The determinations of potash in the crops of each of the four ten-yearly periods showed a very great decline in the yield of potash without any supply; considerably larger amounts, and much less decline, on Plots 12 and 14 with potash residue from the early years, and much larger amounts still where potash was annually supplied. Indeed, according to the figures showing the balance of supply and removal, it would be judged that the whole of the potash residues, from the first eight years' applications on Plots 12 and 14, were at the end of the succeeding forty years approximately exhausted. But it must be remembered that when referring to Dr. Dyer's results on the barley soils, it was pointed out that even his hydrochloric acid extract did not show more than two-thirds of the estimated accumulation of potash. If, then, the excess of potash taken up by the wheat crops on the plots where there was a potash residue were to be attributed to that residue, it would appear that the wheat plant had, during the forty years, taken up more of the accumulated residue than would be susceptible to hydrochloric acid extraction at any one time. Obviously, however, liberation, both of the original and accumulated potash of the soil, would be going on from year to year by weathering, aided probably by the action, in the one case of the sodium, and in the other of the magnesium, salt, annually applied. At any rate, it would seem that Dr. Dyer would find some new points of interest in the investigation of the experimental wheat soils, for from the illustrations given it was evident that we have the conditions of effective residue as well as those of mere exhaustion and accumulation. The suggestion that Dr. Dyer should obtain specimens of a variety of soils from Rothamsted of which the manure and crop history was known, for the purposes of his in-

vestigation, originated, he believed, with our president; and he might say that Sir John Lawes and he were always very glad that the collection of samples at Rothamsted, with their long definite history, should be turned to good account by others, for the investigation of points which they had not time to take up.

Mr. Warington said that, as a contribution to the literature of the subject, he might mention that E. Peters, in 1866 determined the phosphoric acid soluble in water, carbonic water, dilute acetic acid, and hydrochloric acid, in four soils; he concluded that the phosphoric acid in soil was chiefly combined with ferric oxide and alumina. In the same year the speaker showed (*Journ. Chem. Soc.*, 1866, 315) that hydrated ferric oxide or alumina completely decomposed a solution of tricalcium phosphate in carbonic water, the phosphoric acid being taken up while the lime remained in solution; he subsequently showed (*ibid.*, 1868, 1) that soils acted on such a solution in a similar manner. There was, in fact, no doubt that in most soils the phosphoric acid exists as a basic ferric phosphate, and that the great insolubility of soil phosphates is due to this cause.

Dr. Dyer did not refer to Grandeau's view, that the available phosphoric acid and bases in a soil are in combination with humus, and that by acidifying a soil and then extracting with ammonia, the whole of the matters so combined may be obtained in solution and estimated. Nor did he mention Schlœsing's method of extracting the available potash, by agitating the soil with water to which small quantities of nitric acid are added from time to time till a distinct permanent acidity is reached. Nor Petermann's use of an alkaline ammonium citrate to discriminate between the phosphoric acid belonging to the rock from which the soil was formed and that arising from manure.

If the difficulties in the determination of the acidity of root sap are similar to those met with in determining the acidity of lemon-juice and wine lees (*Trans. Chem. Soc.*, 1875, 929, 937, 966), the result will depend a good deal on how the experiment is conducted. If the roots are dried, the acidity found may be below the truth, as the fixed organic acids will decompose chlorides and other salts of volatile acids during drying. It might be well to determine the amount of *active* acid, that, for instance, which is capable of decomposing calcium or magnesium carbonate, rather than the total acidity shown by neutralising with soda, which is sure to be a larger figure. It also appears desirable that the amount of combined organic acid should be determined.

The acidity of the various specimens of root sap exhibits considerable variations, the meaning of which is at present obscure. In one instance the result is certainly not what we should expect. Seven determinations in the sap of turnip and swede roots give a mean of 0·55 per cent of acid, reckoned as citric; while seven determinations in the case of mangel and beet give 0·50 per cent. We should have expected the latter crops to have far surpassed the former in acidity, as mangels are well able to appropriate the combined phosphates of the soil, and stand in no need of phosphatic manure, while the turnip crop is of an exactly opposite character. Mangel leaves are known to contain soluble oxalates.

If agricultural chemists agree to accept a 1 per cent solution of citric acid as the agent in determining the available mineral plant food in a soil, a difficulty will arise when working on soils containing calcium carbonate or other easily acted on base, as in this case the citric acid will be neutralised and weakened. In such cases more citric acid might be added if the amount present never exceeded 1 per cent, and finally reached that point; but we should clearly in this case be acting on the soil with a mixture of citric acid and a citrate.

The question whether free citric acid, or a citrate, or a mixture of both, should be used as solvent is decided by Dr. Dyer in favour of citric acid; the evidence, however, seemed to point to a mixture of both as most satisfactory. Some combined organic acid is doubtless present in the root sap, and this quantity must be continually renewed by the action of this sap on the bases in the soil. Dr. Dyer, at the close of his paper, compared the action of citric acid and of ammonium citrate on a large series of phosphates. It appears that the action of ammonium citrate on many calcium phosphates is too little; but, on the other hand, surely the action of the free citric acid was in these cases too great. It was certainly contrary to our present experience to suppose that 100 lbs. of powdered apatite would supply 12 lbs. of "soluble phosphate" to a crop, which is the result shown by attacking it with 1 per cent free citric acid. Full justice was not done to Wagner's proposal to use a solution containing 10 grms. of free citric acid and 150 grms. of combined citric acid per litre, the solution when used to be *diluted to one-fifth.* A solution of this formula was selected by Wagner after many trials because the proportions of soluble phosphate it yielded with certain typical phosphates were practically the same as the proportions of available phosphate found by actual experiments with these phosphates as manure for plants.

On turning to the results obtained by Dr. Dyer on treating the Rothamsted experimental barley soils with a 1 per cent citric acid solution, we find that this agent succeeds very well in discriminating between the natural phosphates and potash of the soil and the residues of phosphatic and potassic manure; but its action does not exactly correspond to that of the barley roots. The citric acid is, in fact, a better solvent for phosphates, and a worse solvent for potash, than the barley roots. In 1889 the barley crop showed a deficiency of 13 bushels in the absence of phosphatic manure, although citric acid showed the presence of 152 lbs. of soluble phosphoric acid per acre. The barley crop, on the other hand, showed no deficiency due to the absence of potash, although citric acid showed only 57 lbs. per acre. The case becomes stronger when it is recollected that a barley crop takes up more potash than phosphoric acid.

It is shown in the paper that nearly the whole of the excess of phosphoric acid applied as superphosphate is found soluble in hydrochloric acid in the first 9 in. of soil, and that about one-half of this amount is soluble in citric acid. On the other hand, of the excess of potash applied as potassium salts, only two-thirds remains soluble in hydrochloric acid in the first 9 in., and of this quantity a little more than one-third is soluble in citric acid. The case is entirely altered when we come to the farmyard manure plot. According to the published estimate of the composition of the farmyard manure, this plot receives about one-fifth more phosphoric acid than is applied as superphosphate, and more than twice as much potash as is applied as potassium salts. We find, however, in the first 9 in. of the farmyard manure plot less phosphoric acid than where superphosphate has been used, the deficiency per acre amounting to about 1000 lbs. If we regard the potash the result is still more striking, the percentage of potash soluble in citric acid being no greater than where less than half the amount of potash had been applied as potassium salts, while the potash soluble in hydrochloric acid is less than on any plot save two in the whole field. The calculation per acre shows that, notwithstanding the supposed application of 8930 lbs. of potash per acre, the farmyard manure plot contains less potash soluble in hydrochloric acid than any plot in the field save one. The question certainly calls for investigation. Is the published estimate of the composition of the farmyard manure excessive? Has the large amount of decomposing organic matter on this plot kept the phosphoric acid, and especially the potash, in a soluble form, and carried them into the subsoil? Or has the silica of the straw helped to form insoluble compounds with the potash?

The amounts of total potash, and of potash soluble in hydrochloric acid, did not form a very regular series, and it was difficult to form conclusions from them. Accord-

ing to the figures, the use of nitrate of soda had been attended with a serious loss of potash, which we must suppose to have passed into the subsoil. This point certainly demands further enquiry. The method used by Dr. Dyer to extract the potash soluble in hydrochloric acid does not seem satisfactory, no definite time of digestion being specified. In the official United States method, 5 grms. of soil are digested with 50 c.c. of hydrochloric acid, sp. gr. 1·115, in a stoppered bottle, during forty hours at 100°. In other recognised methods a definite period of digestion is always adhered to.

Mr. LLOYD, referring to experiments which he had had occasion to make with an object similar to that which the author of the paper had in view, said that he had met with the difficulty to which Mr. Warington referred, arising from the presence of varying amounts of chalk in soils; it was, however, overcome by first neutralising the soil. Using decinormal hydrochloric acid, he had found that the method gave useful practical results. He then drew attention to experiments made by the late Dr. Voelcker at Woburn, which showed that phosphate of alumina was a much better fertilising agent than bone phosphate, and pointed out that this result did not agree with Dr. Dyer's conclusion that Redonda phosphate, containing much phosphate of alumina, gave up only 9 per cent, while bone phosphate gave up 100 per cent on treatment with the citric solution.

Dr. J. VOELCKER emphasised the importance of studying the behaviour of soils under a great variety of conditions, and also of using air dried soils, such as Dr. Dyer had operated on, instead of soil dried at 100°, as drying was undoubtedly productive of change.

Mr. HUGHES thought that sufficient value had not been attached by the author to the analysis of soils as hitherto carried on by the old methods. He asked why Dr. Dyer had selected for examination a soil on which a crop specially requiring nitrogen, and not potash or phosphoric acid, had been raised. He questioned the necessity of shaking up so much as Dr. Dyer recommended.

Mr. SIBSON said it was necessary to remember that the available plant food will vary with the order of the crops, the material differences discovered in the acidity of many root saps indicating this, although only one factor amongst those causing the remarkable variations in ability exhibited by plants of acquiring their supply of nutriment, which must obviously complicate any process of estimating available constituents. Another important question was as to the effect of a 1 per cent citric acid solution on the residual phosphoric acid from a previous dressing of superphosphate, which had combined with the oxide of iron in the soil, this being known to possess an inferior fertilising value compared with recently applied phosphate.

Dr. DYER, in reply, thanked Sir Henry Gilbert and Mr. Warington for having supplemented his account of the literature of the subject, and admitted the difficulties advanced by the latter as to the interpretation of the sap acidity figures, and also the possibility that some other solution than the one he had used might, at any rate in some cases, better represent the action of the sap. It was to be remembered, however, that any method that might be adopted must be an arbitrary one, and that the object to be attained was to select the best arbitrary solvent for all-round use in soil analysis. At all events, the 1 per cent solution of citric acid appeared to afford fairly consistent results in the case of the soil examined. The difficulty as to soils rich in carbonate of lime was one which, as Mr. Lloyd pointed out, might be met by using an additional quantity of citric acid corresponding to the carbonate of lime present—a tolerably simple matter.

With regard to the apparent relative power of the barley roots to assimilate phosphoric acid and potash, to which Mr. Warington had alluded, it was no doubt a fact that in face of a comparatively small quantity of soluble potash indicated on certain plots, the crop suffered far less than on the phosphoric-acid starved plots, although the actual quantity of soluble phosphoric acid in the latter exceeded that of the soluble potash on the potash-starved plots. But in the text of the paper it was pointed out that the samples of soil were drawn in the autumn, just after the crop had withdrawn its yearly share of available potash, and before the winter had done its work of "weathering"—always assumed to be of great importance in the liberation of natural potash.

The small quantity of phosphoric acid and potash found in the farmyard manure plots was, no doubt, strikingly small compared with the estimated additions and theoretical accumulations. Possibly, as Mr. Warington suggested, the estimates of addition in manure might be too high, but it seemed more probable that on these plots more fertilising matter had been carried downward than in the case of the artificially manured plots. Unfortunately no subsoil samples had been taken, so that what had occurred below the top 9 inches was fo far unknown.

The figures for total potash, representing chiefly undecomposed potassic minerals (such as felspar, &c.), corresponded to such enormous quantities of potash (frequently 1·5 per cent of the dry soil) that comparatively small variations, one- or two- or three-tenths per cent, such as would occur in different parts of the same field, altogether upset and overwhelmed the minor differences in presumably "available" potash, and were of very small significance. Nor did he attach much importance to the solubility in hydrochloric acid; it was, as he had pointed out, largely a function of the quantity of acid used and the time of digestion. The results might, perhaps, have been more consistent had he taken more than 10 c.c. of strong acid for 10 grms. of soil, a quantity which Mr. Warington thought too small, though it was to be remembered that after this had been slowly evaporated off on a water-bath, 10 c.c. more of strong nitric acid were used. But seeing that even this quantity of acid extracted tons of potash per acre from soil practically shown to be now suffering from potash starvation, it did not seem to matter whether a little more or less were got out. What the results, however, did seem to show was that the quantity of potash soluble in hydrochloric acid was apparently a useless and unreliable datum in soil analysis—useless, perhaps, in cases of extreme richness or extreme poverty.

With regard to the question asked by Mr. Hughes, the barley field had been chosen because both its history and the yield of its various plots indicated both the phosphatic and potassic starvation and repletion in various phases, though no doubt if, under the same conditions, a turnip field dould have been selected, it would have been preferable. There was obviously room for a great deal more work in the same direction; he was at present engaged in examining the Rothamsted wheat soils.

The PRESIDENT said that Dr. Dyer's paper undoubtedly dealt with a subject of great interest, the determination of available as distinguished from total mineral plant food being obviously of great importance, not only as a means of arriving at estimates of the fertility of soils, but also in dealing with that very difficult question—the value of unexhausted improvements. All methods devised to such an end were necessarily empirical, and their value would only be ascertained after long experience; were it not that the Rothamsted soils afforded the means of testing the conclusions arrived at, it would be difficult to say whether Dr. Dyer's method was a good one for practical purposes and in advance of those previously suggested; the results Dr. Dyer had arrived at were, however, of a character which a knowledge of the soils examined appeared to justify. He knew, said the President, from conversation with Sir John Lawes, that this was Sir John's view; and, moreover, that Sir John Lawes took the greatest interest in the work, and was of opinion that the prosecution of the inquiry on lines such as were indicated in the paper was of the greatest importance to agricultural science. Whatever the ultimate opinion as to the value of the method advocated by Dr. Dyer, his paper would have the effect of calling attention to the subject, and to the opportunities it afforded for research. It was

important that chemists who desired to study these problems should realise what a mine existed at Rothamsted from which information could be gathered by all who were prepared to patiently devote themselves to enquiries such as Dr. Dyer had indicated; there—and nowhere else in the world—soils were at disposal, awaiting examination, the history of which, during the past fifty years, was accurately recorded, and such an opportunity ought not to be neglected.

115. "*The Behaviour of the more Stable Oxides at High Temperatures.*" Part II. By A. A. Read.

The author has heated the more stable oxides at a temperature of about 1750°, and records the extent to which decomposition (if any) occurred at that temperature. He finds that Sb_2O_5 is converted into Sb_2O_3, V_2O_5 into V_2O_3, Fe_2O_3 into Fe_3O_4, and that the oxides of cobalt and nickel give up the whole of their oxygen, being reduced to the metallic state. In the case of molybdic oxide, uranium trioxide, and stannic oxide, a slight loss of oxygen occurred. The oxides CaO, SrO, BaO, MgO, ZnO, CdO, Al_2O_3, In_2O_3, Di_2O_3, CeO_2, ZrO_2, TiO_2, PbO, Bi_2O_3, Nb_2O_5, Ta_2O_5, and WO_3 were unaltered.

116. "*The Stability of the Oxides Considered in Relation to the Periodic Law.*" By G. H. Bailey, D.Sc., Ph.D.

Taking the temperature of decomposition as an index of stability, the author arrives at the following generalisations as to the stability of the typical oxides in relation to the atomic weights of the elements from which they are derived:—

1. That in the *even* series the oxides are *more* stable the higher the atomic weight.
2. That in the *odd* series they are *less* stable the higher the atomic weight.

He then proceeds to consider the extent to which the various elements combine with oxygen, and draws the conclusions—

1. That in the even series the higher the atomic weight, the greater *in extension* is the tendency to combine with oxygen.
2. That in the odd series there is little tendency to form peroxides, but such as exist show that the tendency to form such oxides *decreases* as the atomic weight rises.

He is of opinion that the diametrically opposite bearing of the odd and even series in regard to the stability of the oxides is an indication that the attraction for oxygen is influenced by the magnetic state of the elements, those of the even series being usually regarded as paramagnetic, and those of the odd series as diamagnetic.

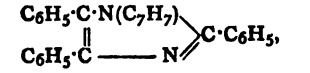
117. "*Interaction of Benzil and Benzylamine in Presence of Zinc Chloride.*" A Preliminary Note. By Francis R. Japp, F.R.S., and W. B. Davidson, M.A., B.Sc.

When benzil, benzylamine, and zinc chloride are heated together at 100°, a product is obtained from which the authors have isolated three compounds: (1) tetraphenylazine, $C_{28}H_{20}N_2$ (melting-point 246°); (2) a compound melting at 164°, and having the formula $C_{28}H_{22}N_2$; and (3) a double compound of an organic chloride with zinc chloride, which is deposited from its alcoholic solution, on the addition of ether, in lustrous crystals of the formula $(C_{35}H_{29}N_2Cl)_2ZnCl_2,3(C_2H_5)_2O$, melting at 248°.

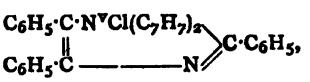
When exposed to the air, these crystals give off their "ether of crystallisation." The chloride $C_{35}H_{29}N_2Cl$, when isolated from the zinc compound, forms prisms which, when rapidly heated, melt at 253°.

The compound $C_{28}H_{22}N_2$ is a tertiary amine, and unites directly with benzyl chloride to form the chloride $C_{35}H_{29}N_2Cl$, which is therefore a quaternary ammonium chloride.

Suspecting that these two compounds might be benzyl-derivatives of lophine, the authors heated lophine with benzyl chloride, and found that the same two substances were formed in the interaction. The compound $C_{28}H_{22}N_2$ is, therefore, *benzyllophine*,



and the chloride $C_{35}H_{29}M_2Cl$ is *dibenzyllophinium chloride*,



the latter corresponding with Kühn's diethyllophinium iodide.

The following equations express the formation of the two compounds:—

1. $C_{14}H_{10}O_2+2C_6H_5\cdot CH_2\cdot NH_2=C_{28}H_{22}N_2+2H_2O+H_2$.
2. $2C_{14}H_{10}O_2+6C_6H_5\cdot CH_2\cdot NH_2+ZnCl_2=$
$=2C_{35}H_{29}N_2Cl+2NH_3+Zn(OH)_2+2H_2O+2H_2$.

These compounds yield the platinichlorides—

$(C_{28}H_{22}N_2,HCl)_2PtCl_4$ and $(C_{35}H_{29}N_2Cl)_2PtCl_4$.

The authors propose to ascertain whether a similar interaction occurs with other primary amines of the formula $R'\cdot CH_2\cdot NH_2$ and other diketones.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, March 5, 1894.

Sir James Crichton Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members of the Royal Society:—Edward Henry Cardwell, James Childs, J. Dundas Grant, M.D., F.R.C.S., Sir Alfred Seale Haslam, Alexander T. Hollingsworth, Robert Trefusis Mallet, M.Inst.C.E., Sidney Ashmore Stewart Maud, Mrs. Hermina Melchers, Percy Alport Molteno, B.A., LL.B., Dr. Eugen Obach, Charles E. S. Phillips, The Hon Lionel Walter Rothschild, Miss Harriett Russell, J. Craneñeld Scholey, Miss Ida Stewart, Arthur Talbot.

The special thanks of the Members were returned to Mrs. Rae for her present of a Portrait of the late Dr. John Rae.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

INSTITUTE OF CHEMISTRY.

The Eighth Annual General Meeting of the Institute of Chemistry of Great Britain and Ireland (incorporated under Royal Charter) was held on Thursday, March 1st, at the Offices of the Institute, 30, Bloomsbury Square, London, W.C.

The annual accounts and the Report of the Council for the past year were received, and Dr. W. A. Tilden, F.R.S., the retiring President, delivered an Address in which he referred to the progress of the Institute during the three years of his presidency.

The Officers and Council for the ensuing session were elected, Dr. W. J. Russell, F.R.S., of St. Bartholomew's Hospital, succeeding Dr. Tilden as President of the Institute.

Notwithstanding the fact that the Institute has to lament the loss of eight Members by death and fourteen from other causes, the number of Members has increased by nineteen during the past year, and ninety-eight Students have been admitted.

The Register now contains 738 Fellows, 109 Associates, and 207 Students.

NOTICES OF BOOKS.

Essays in Historical Chemistry. By T. E. THORPE, Ph.D., B.Sc. (Vict.), Sc.D. (Dubl.), F.R.S., Professor of Chemistry in the Royal College of Science. London and New York: Macmillan and Co.

DID we set out to discuss or even to notice every important passage in this interesting work, we should find ourselves committed to the production of a goodly volume.

Dr. Thorpe gives in a series of thirteen chapters biographical essays on some of the most eminent chemists, from the birth of the Royal Society down to our own time.

He begins with Robert Boyle, styled in an inscription the Father of Chemistry, and the brother of the Earl of Cork. We learn something about the anathemas vented against the Royal Society by Henry Stubbe, Hobbes, Butter, and others, most of whom are remembered only for their folly.

But in the midst of this hubbub Science even became fashionable, and the King set up a laboratory. It is interesting to know that Boyle made experiments on living animals, and were he yet surviving he would be duly execrated in Bestiarian circles. He is here pronounced "inferior only to Bacon and Newton," a high, but not unmerited compliment. It is painful, however, to find that his law is in most Continental, or at least French treatises, ascribed to Mariotte.

Next follows a biography of Joseph Priestley. Had he followed the advice of Edward Gibbon he would not merely have escaped the persecutions which befel him, but would have been able to do more for science. The most suggestive feature in his after-career is his obstinate defence of phlogiston after he had, by the discovery of oxygen, supplied the decisive evidence against it.

The life of Scheele brings to light the fact that in this epoch-making discovery he had anticipated Priestley by at least a year. We have proof that Scheele's researches on oxygen were made partly before the autumn of 1770, and partly prior to 1773. By a variety of untoward circumstances, his memoir on "Air and Fire" did not appear until 1777. The publisher, Swedenes, is chiefly to blame. We have, however, no reason to suspect that any hint of Scheele's results had reached Priestley. Those who seem to regard profound mathematical knowledge as to be demanded from all chemists may learn a lesson to the contrary from the brilliant career of Scheele—a career rendered all the more difficult by poverty, a feeble constitution, and a short life.

Henry Cavendish, to whom our notice is next called, is remarkable as a man in whom the passions and emotions were atrophied. His being was pure intellect; he lived merely to study and discover; and that not for any honour which might accrue to himself. When he had completed an investigation and drawn up an account of the results, he often left the papers to lie unpublished for years. Had he given his researches to the world, the advance of science would have been much expedited, and the world would have had a fuller knowledge of his greatness. It is now generally admitted that his claims as the discoverer of the composition of water cannot be gainsaid. Says Dr. Thorpe: "If the claim of anyone to be styled the founder of chemistry as a science rests upon his recognition of its quantitative relations, may we not also, and with equal truth, say that chemistry is an English science — its founder was Cavendish, of immortal memory?" Cuvier, in pronouncing his official *éloge* before the French Academy, said: "He has been so fortunate or so prudent that we find in his history no other incidents than discoveries."

Very different was the case with Antoine Laurent Lavoisier. Of his judicial murder the particulars are so well known that we scarcely need even add an execration to the memories of Coffinhall, "the brutish idiot" who declared that "the republic has no need of men of science," or of the traitor Fourcroy. We must not forget that the crime for which Lavoisier was put to death was not his scientific fame, but the fact of his having been a member of the *Ferme Général;* but we must also remember that his enemies aimed at and effected the suppression of all the scientific societies of France. In this mad task they had the co-operation of the artist David, and of Marat, who traduced him along with La Place, Monge, and Cassini, and denounced him in the *Ami du People* in language for which the dagger of Charlotte Corday was too honourable a punishment. Afterwards a solemn funeral ceremony in honour of Lavoisier was decreed by the Directoire at which Fourcroy had the meanness to pronounce an *éloge*.

The biography of Faraday is at once interesting and painful—painful for the unpleasant light it throws on one whom we should otherwise wish to revere. It will scarcely be believed that Davy, from whatever motive, was annoyed at the election of his former assistant as a Fellow of the Royal Society; that he walked for an hour round the courtyard of Somerset House arguing that Faraday ought not to be elected; that he threatened to take down Faraday's certificate! At the ballot there was only *one* black ball, the giver of which may be suspected.

The remainder of this valuable work, which lack of space does not allow us to examine, is taken up with accounts of Graham, of Wöhler, Dumas, Kopp, of Mendeleeff, and with an account of the rise and development of synthetical chemistry.

We most strongly recommend Dr. Thorpe's work not merely to students of chemistry, but to all men and women of culture.

Treatise of Mineral Analytical Chemistry. ("Traite de Chimie Analytique Minerale Qualitative and Quantitative"). By L. L. DE KONINCK, D.Sc., Professor of Chemistry at the University of Liége. 8vo., pp. 1064, with 163 Figures and a Coloured Plate in the First Volume, and 85 Figures in the Second. Liége: Mierstrasz. 1894.

THE work before us is supplied with a preface unusually long, and perhaps discursive, but containing much worth the attention of the student. To show precisely his point of view he compares the titles *Lehrbuch* and *Handbuch* so commonly borne by German scientific works. The "Lehrbuch," or text-book, is a theoretical treatise having its place in the library or the office. The "Handbuch," or manual, is of a more practical character, and belongs to the laboratory table.

Dr. de Koninck aims at producing rather a text-book than a manual. He states that in his work theory occupies a place relatively more considerable than it does in the works of Rose, Fresenius, Mohr, or Bunsen. He seeks to generalise as much as possible rather than to specialise. He complains that the terms "method" and "procedure" are too often confounded, to the former of which he assigns a more general acceptation than to the latter.

In his advice to students and to junior experts he, like Fresenius, lays particular emphasis on "*scrupulous conscientiousness.*" He urges that the two branches of analysis, the qualitative and quantitative, should be studied side by side. Dr. de Koninck considers that whilst quantitative operations are preferable for the cultivation of manipulative skill, qualitative research affords the better intellectual training. He states that with time and patience we may get very exact determinations executed by ignorant boys, but we can never entrust them with serious qualitative investigations. We have often thought that the typical laboratory boy would make a novel and—to outsiders—entertaining figure in the literature of the day.

A caution is given to mistrust processes arrived at deductively without actual experiment. Some reactions

which are exact when applied to pure substances existing in a separate state, sometimes lead the operator greatly astray if they are applied to a mixture of the same substances. Thus, no less eminent an analyst than H. Rose, observing that barium sulphate is not affected by a solution of ammonium carbonate, which converts strontium sulphate entirely into strontium carbonate with formation of ammonium sulphate, proposed this reaction as a means of separating barium from strontium. But on actual experiment it was found that a part of the strontium salt escaped decomposition, whilst the barium salt was partially attacked, so that the total error amounted in some cases to 80 per cent!

We are much pleased to find an honest and outspoken condemnation of the Baumé hydrometer, still so much employed in France, and universally in vogue in America.

A strange oversight has been committed on p. 261. In speaking of the Nessler test for minute quantities of ammonia the author ascribes its quantitative modification to Frankland and Armstrong, instead of to Wanklyn. The method which the two former chemists have devised for the determination of organic nitrogen in water is a combustion process, as may be found detailed in any manual of hygienic analysis.

The methods here expounded are the gravimetric, volumetric, gasometric, colorimetric, densimetric, and polarimetric. The spectroscopic, refractometric, and rheostatic procedures are more briefly touched upon.

We can recommend this work to the favourable notice of chemists.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 8, February 19, 1894.

M. E. Maumené solicits the Academy to include him among the candidates for the vacancy in the Chemical Section occasioned by the decease of Prof. Frémy.

A Symmetrical Aplanetic Object Glass.—Ch. V. Zenger.—The author's lenses have the advantage of correcting: 1. The exact achromatism for the entire length of the spectrum. 2. The astigmatism to a great degree. 3. They reduce the spherical aberration for a suitable aperture to the minimum value of one second of an arc. 4. They absolutely correct the curvature of the field.

Minimum Electromotive Force necessary for the Electrolysis of Electrolytes.—Max Le Blanc.—This paper is a reclamation of priority as against M. Nourisson (*Comptes Rendus*, cxviii., No. 4, p. 189).

Fusibility of Isomorphous Mixtures of some Double Carbonates.—H. Le Chatelier.—The author finds that potassium and sodium carbonates, on fusion with barium, strontium, and calcium carbonates, easily yield isomorphous and well-crystallised double salts. Lithium carbonate, in spite of the analogies ascribed to it by the periodic classification, cannot be substituted in these combinations for the true alkaline carbonates. It combines with them, on the contrary, after the manner of the alkaline earthy carbonates.

Allotropic Transformation of Iron under the Influence of Heat.—Georges Charpy.—The author's experiments show that in tempering iron undergoes a transformation which may equally produce hardening in the cold, but they do not indicate that this transformation is the hardening of steel.

Constitution of Orcine.—M. de Forcrand.—A thermochemical paper not adapted for useful abstraction.

Ethylphenols.—A. Béhal and E. Choay.—An account of para-, ortho-, and meta-ethylphenol. The substance known as α-ethylphenol is identical with para-ethylphenol, which has nothing in common with that described by Errera and Auer. Ortho-ethylphenol has a lower boiling-point than that commonly assigned to it; it boils at 202° to 203°. Meta-ethylphenol is a liquid boiling at 214° and having at 0° the specific gravity 1·0403.

Multirotation of Sugars.—P. Th. Muller.—The correlative reaction of the multirotation of sugars makes part of the reactions, said to be of the first order, and is governed by the law of active masses.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., No. 3.

A Congress of learned Societies is announced as to be opened on March 27 at 2 p.m.

Cryoscopy of the Hydrate $SO_4H_2H_2O$.—R. Lespieau.—We have here a substance which melts in its water of crystallisation, and behaves, from a cryoscopic point of view, like the ordinary solvents, both experimentally and theoretically, *i.e.*, it obeys the laws of Raoult and van 't Hoff. The author calls to mind that if the acid combines with the dissolved substance, the observations are not interfered with.

Researches on the Chemical Action of Abrastol (Calcium Naphthylsulphate) upon Wine.—Scheurer-Kestner.—Contrary to what has been announced, abrastolised wine does not contain any traces of sulphuric acid. Beside the harmless naphthyl sulphate, abrastol does not introduce any novel element into wine. Abrastol may supersede "plastering" in wines with hygienic advantage. It introduces only 0·0363 grm. per litre, as against 2 grms. introduced by plastering. Abrastol has the advantage of being easily detected to the extent of 1-40,000th part.

Microbicide Action of Gallanilide or Gallanol.—P. Cazeneuve.—The author concludes that gallanilide in excess completely arrests the life of micro-organism. In a weak solution (1 part per 1000) it diminishes the vegetability of anthrax and of staphylococcus, arrests that of the bacillus of Eberth, but has no influence upon the pyocyanic bacillus and that of the *bacillus coli*. In a very weak solution (1 part per 5000) it does not arrest all the vegetability of the micro-organisms, but it completely destroys all pathogenous power. A little of the powder of gallanilide added to a culture broth rapidly destroys the bacillus of cholera. It is not poisonous if introduced into the digestive canal even to the extent of 5 grms. in powder. If injected into the blood in an alkaline solution it is poisonous.

Researches on the Homologues of Gallanilide; Preparation of Galloparatoluide, of its Triacetylated Derivative, and some of its Salts.—P. Cazeneuve.—The preparation of gallanilide by the reaction of aniline upon tannin led us to think that by using the homologues of aniline we should obtain the homologues of gallanilide by a fission analogous to that of the tannin of gall nuts. Experiment has shown that only paratoluide gives a derivative by fission under these conditions.

Oxindophenolic Colouring Matters Derived from Gallanilide and Galloparatoluide.—P. Cazeneuve.—An account of gallocyanine, prune, and tannin-indigo.

Formation of Mannite in Wines.—H. and A. Malbot.—The authors give a history of observations relative to the presence of mannite in fermented liquids.

Zeitschrift fur Analytische Chemie.
Vol. xxxii., Part 5.

Characteristics of Flame.—A. Smithells and H. Ingle.—From the *Journal of the Society of Chemical Industry.*

Improvements in Balances.—A number of papers by A. Stift (*Ungar. Zeit. Zucker Industrie*) and R. Penksky (*Instrumentenkunde*). These papers require the accompanying illustrations.

A Universal Gas-Volumeter.—G. Lunge (*Zeit. fur Angewandte Chemie*).—This paper also requires the accompanying figures.

Viscosimeters for Oils.—Already inserted.

Filtration with an Inverted Funnel.—A. Unguer (*Zeit. fur Angewandte Chemie*).—The mouth of the funnel is turned downwards and covered with filter-paper, over which is tied a protective tissue. To this end the funnel is provided with a projecting edge.

An Appliance for Filtration in Heat.—Th. Paul (*Ber. Deutsch. Chem. Gesell.*).—An illustrated paper.

Filter-paper Freed from Grease.—Schleicher and Schüll (*Pharm. Centralhalle*).—This paper is specially prepared for milk analysis according to the Adams process. It contains only 0·025 per cent of fatty matter, whilst unprepared paper contains as much as 0·66 per cent.

An Agitator for Superphosphates.—A. Keller (*Zeit. fur Angewandte Chemie*).—An illustrated memoir.

Several Drying Closets.—Max Kähler (*Chemiker Zeitung*).—This paper requires the three accompanying figures.

Gas Furnaces for Laboratory Use (*Berg. und Hütten Zeitung*).—An account of certain crucible furnaces introduced by Muencke, Rössler, and Issem.

Production of a Long-continued Current of Carbonic Acid.—R. Ulhricht and O. Förster (*Chemiker Zeitung*).—The apparatus is very similar to that of Pollock and Wilde, and has the advantage of completely utilising the acid.

A Simple Refrigerator and Extractor.—K. Farnsteiner (*Chemiker Zeitung*).—An illustrated paper.

Extraction Appliances for Liquids.—A. Smetham.—From the *Analyst.*

A Gas-absorption Apparatus.—G. L. Norris.—From the *Journal of Analytical and Applied Chemistry.*

A Compendious Apparatus for the Production of Distilled Water.—G. W. James (*Journal of Analytical and Applied Chemistry*) and A. Von Kaleczinsky (*Chemiker Zeitung*).—The latter of these papers is illustrated.

Refrigeration Battery for Distillation and Cohobation.—K. Zulkowsky (*Zeit. fur Angewandte Chemie*).—Requires the two accompanying figures.

Preservation of a Constant Level in Water-baths and for the Extinction of the Flame in a Dried-up Water-bath (*Chemiker Zeitung*).—Already inserted.

Preservation of the Projection of Mercury in Determinations of Nitrogen.—Liechti (*Chem. Centralblatt* and *Pharm. Centralhalle*).—The paper requires the accompanying figure for intelligibility.

Applications of Aluminium for Laboratory Uses.—G. Bomemann (*Berichte der Deutsch. Chem. Gesell.*).—The author shows the advantages of aluminium as compared with other metals, especially sheet-copper. He points out its resistance to sulphuretted hydrogen, hot and moist air, sulphuric and nitric acids, and the organic acids, its low specific gravity, its high specific heat, and its good conductivity for heat and electricity. He compares an air-bath of aluminium during heating and cooling with a copper air-bath, showing that the former is more easily heated and effects a more uniform internal distribution of heat. The metal remains perfectly bright, and after being in use for three months it shows only a very slight whitish coating. The exfoliation noticed in copper does not occur here. The coating consisted of alumina or basic aluminium sulphate. The metal is scarcely attacked within by the action of boiling water. After use for three weeks a loss of weight could not be recognised. Rings and clamps as supports proved satisfactory. Sand-baths and crucibles of aluminium cannot be recommended, as they are softened at 500°. Chimneys for burners and funnels for hot water were satisfactory.

Several Laboratory Appliances.—F. A. Gooch.—From the *American Journal of Science.*

Purification of Mercury.—W. Jäger (*Annalen der Physik und Chemie*).—The metal is submitted to a double distillation *in vacuo*, avoiding oiled cocks and caoutchouc joints, and purified by electrolysis in order to eliminate electro-positive metals.

Determination of the Specific Gravity of Sulphuric Acid.—H. D. Richmond.—From the *Journal of the Society of Chemical Industry.*

Preparation of Solution of Stannous Chloride.—Hirsch-Schneider (*Pharm. Centralhalle*).—The author sets out with tin-crystals, his object being merely to obtain a solution directed in the German Pharmacopeia as a reagent for arsenic.

Preparation of Pure Chloroform from Salicylid-Chloroform or Orthohomosalicylid Chloroform.—R. Anschütz (*Liebig's Annalen*).—Both salicylide and orthohomosalicylide form with chloroform compounds which crystallise well. In them the chloroform is in a state of unstable combination and escapes at a gentle heat.

Impurities of Zinc used for Reduction in Determinations of Iron and Phosphorus.—F. L. Crobough.—From the *Journal of Applied Chemistry.*

MEETINGS FOR THE WEEK.

MONDAY, 12th.—Society of Arts, 8. (Cantor Lectures). "The Decorative Treatment of Artificial Foliage," by Hugh Stannus, F.R.I.B.A.

TUESDAY, 13th.—Royal Institution, 3. "Locomotion and Fixation in Plants and Animals," by Prof. Charles Stewart, Pres.L.S.
—— Medical and Chirurgical, 8.30.
—— Institute of Civil Engineers. 8.
—— Photographic, 8.

WEDNESDAY, 14th.—Society of Arts, 8. "The Fountain Air Brush," by Charles L. Burdick.
—— Pharmaceutical, 8.

THURSDAY, 15th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "The Vendânta Philosophy," by Prof. Max Müller, M.A.
—— Chemical, 8. "The Action of Hydroxylamine on Formic Aldehyd," by Prof. Dunstan, F.R.S., and Dr. A. Bossi.

FRIDAY, 16th.—Royal Institution, 9. "The Scientific Work of Tyndall," by the Right Hon. Lord Rayleigh, F.R.S.
—— Quekett Club, 8.

SATURDAY, 17th.—Royal Institution, 3. "Light, with special reference to the Optical Discoveries of Newton," by the Right Hon. Lord Rayleigh, F.R.S.

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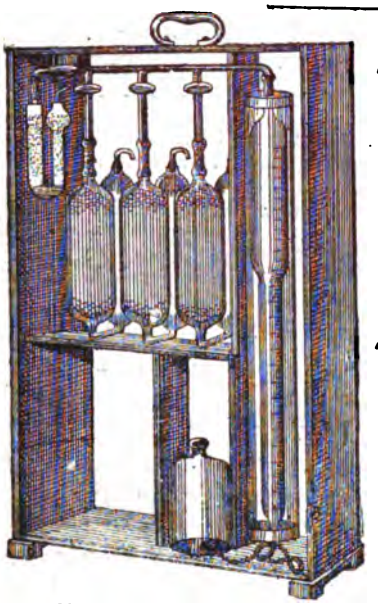

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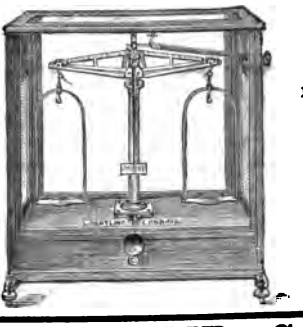

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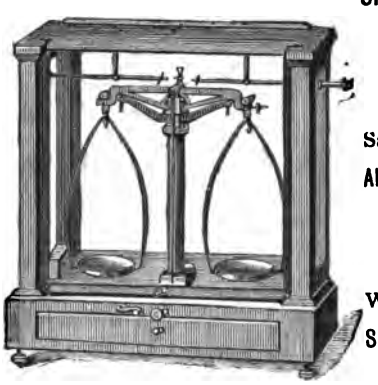

FIG. 3*a*.

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ON THE

RELATIONS BETWEEN THE VISCOSITY (INTERNAL FRICTION) OF LIQUIDS AND THEIR CHEMICAL NATURE.*

By T. E. THORPE, D.Sc., F.R.S., and J. W. RODGER, Assoc. R.C.S.

The purpose of this paper is to throw light upon the relations between the viscosity of homogeneous liquids and their chemical nature. It is divided into three parts. Part I. contains a summary of the attempts which have been made, more particularly by Poiseuille, Graham, Rellstab, Guerout, Pribram and Handl, and Gartenmeister, to elucidate this question. Although it is evident from the investigations of these physicists that relationships of the kind under consideration do exist, it must be admitted that they are as yet not very precisely defined, mainly for the reason that the conditions by which truly comparable results can alone be obtained have received but scant consideration.

For example, it seems futile to expect that any definite stoichiometric relations would become evident by comparing observations taken at one and the same temperature. Practically, nothing is known of a quantitative character concerning the influence of temperature on viscosity.

From the time which a liquid takes to flow through a capillary tube under certain conditions, which are set out at length in the paper, a measure of the viscosity of the liquid can be obtained.

An apparatus was, therefore, designed on this principle which admitted of the determination in absolute measure of the viscosity, and for a temperature range extending from 0° up to the ordinary boiling-point of the liquid examined. In this way, instead of finding, as has been the usual custom, relative times of flow in the same apparatus under the same external conditions of temperature and pressure, and which might or might not be taken as measures of a single physical magnitude of the substance, *i.e.*, its viscosity, the physical magnitude itself could be measured, and the various influences which are found to affect its value could be allowed for. The physical constants thus obtained could then be treated from the point of view of the chemist, and the comparison would then be of the same kind as that employed in connection with other physical magnitudes.

Full details of the conditions determining the dimensions of the apparatus and of the modes of estimating these dimensions, together with the methods of conducting the observations, are given in the paper.

The corrections to be applied to the direct results are then discussed.

The question of the mathematical expression of the relation of viscosity of liquids to temperature is considered, and reasons are given for preferring the formula of Slotte—

$$\eta = c/(1+bt)^n;$$

η is here the coefficient of viscosity in dynes per square c.m., and c, b, and n are constants varying with the liquid.

With a view of testing the conclusions set out at length in the historical section of the paper, and, in particular, of tracing the influence of homology, substitution, isomerism, and, generally speaking, of changes in the composition and constitution of chemical compounds upon viscosity, a scheme of work was arranged which involved the determination, in absolute measure, of the viscosity of some seventy liquids, at all temperatures between 0° (except where the liquid solidified at that temperature) and their respective boiling-points.

Part II. of the memoir is concerned with the origin and modes of establishing the purity of the several liquids; it contains the details of the measurements of the viscosity coefficients, together with the data required to express the relation of viscosity coefficients to temperature by means of Slotte's formula, and tables are given showing the agreement between the observed and calculated values.

In Part III. the results are discussed. In the outset the factors upon which the magnitude of the viscosity probably depends are dealt with. The influence of possible molecular aggregations, as indicated by observations of vapour densities, boiling-points, and critical densities, and, more especially, by measurements of surface energy, made by Eötvös in 1886, and more recently by Ramsay and Shields, are taken note of.

The deductions which may be made by considering the graphical representation of the results, showing the variations of viscosity coefficients with temperature, are then set forth.

For liquids which probably contain simple molecules, or for which there is little evidence of association of molecules at any temperature, the following conclusions may be drawn:—

1. In homologous series the coefficient of viscosity is greater the greater the molecular weight.
2. An iso-compound has always a smaller viscosity coefficient than the corresponding normal compound.
3. An allyl compound has, in general, a coefficient which is greater than that of the corresponding isopropyl compound, but less than that of the normal propyl compound.
4. Substitution of halogen for hydrogen raises the viscosity coefficient by an amount which is greater the greater the atomic weight of the halogen; successive substitutions of hydrogen by chlorine in the same molecule bring about different increments in the viscosity coefficients.
5. In some cases, as in those of the dichlorethanes, substitution exerts a marked influence on the viscosity, and in the case of the dibromides and benzene it may be so large that the compound of higher molecular weight has the smaller viscosity.
6. Certain liquids, which probably contain molecular complexes, do not obey these rules. Formic and acetic acids are exceptions to Rule 1. The alcohols, at some temperatures, but not at all, are exceptions to Rule 2; at no temperatures do they conform to rule 3.
7. Liquids containing molecular complexes have, in general, large values of $d\eta/dt$.
8. In both classes of liquids the behaviour of the initial members of homologous series, such as formic acid and benzene, is in some cases exceptional when compared with that of higher homologues.

As regards the influence of temperature on viscosity, it is found that the best results given by Slotte's formula are in cases where the slope of the curve varies but little with the temperature. From the mode in which the value of the constants n and b are derived, it cannot be expected that their magnitudes will be related in any simple manner to chemical nature. With the exception of certain liquids, such as water and the alcohols, which are characterised by large temperature coefficients, and in which there is reason to expect the existence of molecular aggregates, the formula

$$\eta = c/(1+\beta t+\gamma t^2),$$

obtained from Slotte's expression by neglecting terms in the denominator involving higher powers of t than t^2, gives a close agreement with the observed results, and in this formula the magnitude of β and γ are definitely related to the chemical nature of the substances.

* The Bakerian Lecture of the Royal Society.

In order to obtain quantitative relationships between viscosity and chemical nature, and to compare one group of substances with another, it is necessary to fix upon particular temperatures at which the liquids may be taken as being in comparable conditions as regards viscosity, and to compare the values of the viscosities at those temperatures.

The first comparable temperature which suggested itself was the boiling point.

A second comparable temperature was obtained by calculating values of corresponding temperatures by the method of van der Waals with such data as could be obtained.

The third basis of comparison consisted in using temperatures of equal slope, *i.e.*, temperatures at which the rate of change of the viscosity coefficient is the same for all liquids.

At each of the different conditions of comparisons, the experimental results have been expressed according to the same system, in order to show at a glance relationships between the magnitudes of the viscosity constants and the chemical nature of the substances. The liquids are arranged so that chemically related substances are grouped together. Tables are constructed which give the values of the three different magnitudes derivable from measurements of the viscosity of the substances.

1. Values of viscosity coefficients (η).
2. Values of $\eta \times$ molecular area, *i.e.*, ***molecular viscosity***.
3. Values of $\eta \times$ molecular volume, *i.e.*, ***molecular viscosity work***.

The coefficient η is the force in dynes which has to be exerted per unit-area of a liquid surface in order to maintain its velocity relative to that of another parallel surface at unit distance equal to unity. It seemed, however, that relations between viscosity and chemical nature would best be brought to light if, instead of adopting merely unit areas, areas were selected upon which there might be assumed to be the same number of molecules. The ***molecular viscosity*** is proportional to the force exerted on a liquid molecule in order to maintain its velocity equal to unity under the unit conditions above defined. With the units chosen it is the force in dynes exerted on the molecular area in square centimetres, under unit conditions. The ***molecular viscosity work*** may be regarded as proportional to the work spent in moving a molecule through the average distance between two adjacent molecules under unit conditions. In ordinary units it is the work in ergs required to move a surface equal to the molecular area in square centimetres through the molecular length in centimetres.

In the case of the comparison of the viscosity coefficients at the boiling-point, it is found:—

1. As an homologous series is ascended, in a few cases the viscosity coefficient remains practically the same, but in the greater number of series the coefficients diminish. In one series the coefficients increase; in the case of the alcohols the coefficients vary irregularly with ascent of the series.
2. Of corresponding compounds, the one having the highest molecular weight has in general the highest coefficient (the aliphatic acids, and to a much greater extent the alcohols, do not conform with this rule.
3. Normal propyl compounds have, as a rule, slightly higher values than allyl compounds; in the case of the alcohols, propyl compounds have much the higher value.
4. The effect of molecular weight in some cases may be more than counterbalanced by that of constitution, or of complexity.
5. The lowest members of homologous series frequently exhibit deviations from the regularity shown by higher members.
6. An iso-compound has in general a larger coefficient than a normal compound, and the differences reach their maximum in the case of the alcohols.
7. In the case of other metameric substances, branching in the atomic chain and the symmetry of the molecule influence the magnitudes of the coefficients; the ortho-position, in the case of aromatic compounds, appears to have a more marked effect on the coefficient than either the meta- or para-position. Acetone and ether have coefficients that are less than half the values given by the isomeric alcohols.
8. One of the most striking points thus brought to light is the peculiar behaviour of the alcohols, and to some extent of the acids, as contrasted with that of other liquids.

Comparisons of molecular viscosity at the boiling-point show—

1. That, with the exception of the alcohols, dibromides, and the lowest members of homologous series, an increment of CH_2 in chemical composition corresponds with an increase in molecular viscosity.
2. With the above exceptions, it is also apparent that the corresponding compound having the highest molecular weight has the highest molecular viscosity: the difference in molecular viscosity between the corresponding members of two correlated series is fairly constant.
3. The relationships shown in the other tables are substantially of the same nature as those given by the viscosity coefficients.

The comparisons which give the largest deviation from regularity contain those substances which, as already shown, exhibit a peculiar behaviour, namely, the alcohols, acids, propylene, dibromide, ethylene dichloride, &c.

In order to indicate how molecular viscosity at the boiling-point is quantitatively connected with chemical nature, attempts were made to calculate the probable partial effects of the atoms on the molecular viscosity. Values were also assigned to the effects of the iso-grouping of atoms, the double linkage of carbon atoms, and the ring grouping. The values thus obtained are given in the following table:—

Fundamental Viscosity Constants (Molecular Viscosity at the Boiling-point, in Dynes $\times 10^4$).

Hydrogen	80
Carbon	−98
Hydroxyl oxygen, C—O—H	196
Ether oxygen, C—O—C	35
Carbonyl oxygen, C=O	248
Sulphur, C—S—C	155
Chlorine	284
Bromine (in monobromides)	420
Bromine (in dibromides)	479
Iodine	520
Iso-grouping	15
Double linkage	113
Ring-grouping	610

As regards the meaning to be attached to fundamental viscosity constants in general, the following points may be noted. Viscosity may be taken as a measure of the attractive forces in play between molecules, *i.e.*, of intermolecular attraction. From the fact that an increment of CH_2 in chemical composition, or the substitution of an atom of chlorine, bromine, or iodine for an atom of hydrogen, brings about a definite change in the viscosity, it is evident that intermolecular attraction is really a property of the atoms comprising molecules. But, besides change in molecular weight, change in the mode of grouping of the same atoms also affects the magnitude of the viscosity. The observations show that iso-compounds have values differing from those of isomeric normal compounds; ring compounds have not the values which, by the study of straight chain compounds, they might be expected to have. Compounds containing hydroxyl oxygen give values of the viscosity differing widely from those of compounds containing carbonyl oxygen. The same atoms must therefore exert different effects when differently

linked together. That the effects of all the atoms in the molecule are not altered by change in the mode of linkage is proved by the fact that the effect of CH_2, of iodine, of bromine, &c., is the same in normal and in iso-compounds.

In the present state of the question it is impossible to say what particular atoms are affected by change in the mode of linkage. Hence the method adopted in deducing fundamental constants is to assume that certain atoms retain the same values under all conditions, whilst the change in the values of those atoms which are affected by the mode of linkage is, when possible, expressed either by a new constant—the value of an iso-linkage, a double-linkage, &c., or by saying that a particular atom has assumed a new value, *e.g.*, carbonyl oxygen, hydroxyl oxygen, &c. In some cases the method of calculation may lead to the result that a negative constant is ascribed to a particular atom. In deducing the values of carbon and hydrogen, for example, it is implied that in a CH_2 group and in the molecule of a paraffin the effects of each atom of carbon and hydrogen is the same. The above facts, and the reasoning based upon them, show that this is not the case, and although the absolute effect exerted by each atom upon the viscosity is positive, the fundamental constant of an atom may be negative, as it may involve a constitutive effect, which at present cannot be localised in a particular region of the molecule. For these reasons fundamental constants are to be regarded as empirically ascertained magnitudes, which are merely intended to indicate how far the observed results may be represented as the sum of partial values which are the same for all substances. They have no reference to the possible behaviour of the elements when in the free state; they simply show how far definite changes in chemical nature correspond with definite changes in viscosity.

Tables are given which show the concordance between the observed molecular viscosity and those calculated by means of these constants. In the case of forty-five liquids the difference between the observed and calculated values rarely exceeds 5 per bent. In the case of the isomeric ketones and aromatic hydrocarbons, the differences are in part due to constitutive influences, which cannot at present be allowed for in obtaining the calculated values.

(To be continued.)

THE SOLUBLE ACTION OF TARTRATES ON THE METALLIC HYDRATES.

By H. N. WARREN, Research Analyst.

THE general solvent action that a tartrate, such as Rochelle salt, possesses towards the metallic hydrates and carbonates is, for instance, in the case of ferric and cupric compounds, too well known to need further description. But on a comparison being made with the other compounds of a similar class, or group, a marked assimilation is observed. Not only does the solvent action of Rochelle salt predominate over the ferric and like compounds, but also to an equal extent over the ferrous, dissolving them with great facility, forming a deep green solution; and it is also exercised to a similar extent over the hydrates and precipitates of zinc, manganese, nickel, cobalt, iron, chromium, and aluminium. Even the precipitates of barium, strontium, magnesium, and calcium compounds are to a considerable extent soluble when boiled with a concentrated solution of Rochelle salt. Owing to the ready manner in which antimony oxychloride is dissolved by this salt, I have several times observed demonstrators, when lecturing, advise the use of this compound as a reagent for determining whether the precipitate formed is one of antimony or bismuth, or if both are in admixture. This is, however, entirely erroneous, and is apt to lead a beginner widely astray, since both compounds are entirely dissolved on adding a sufficient quantity, and heating. The same compound is not uncommonly used when a quick method is required to distinguish between a precipitate supposed to be either one of antimony or tin, notwithstanding the entire list of stannic compounds are almost as readily soluble in a solution of this reagent as are the antimonic precipitates. An exception to this rule appears to exist in the case of cadmium carbonate, which is practically insoluble in a neutral tartrate solution. Cadmium compounds, when in solution, may, by suitable means, by this compound be therefore separated from those of the cupric, those of the latter being, as is well known, soluble in excess of that salt.

I have not as yet fully experimented with respect to the solvent action of Rochelle salt on the rarer earths—zirconia, glucina, &c., but am of opinion that it may possibly open an easy means of separating such oxides when in the hydrated condition.

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THE ACTION OF HEAT UPON ETHYLENE.*

By VIVIAN B. LEWES.

(Concluded from p. 112).

As a further step in securing factors by which to trace the decomposition, it seemed advisable to attempt to trace the action of heat upon the benzene vapour formed by the polymerisation of the acetylene; and in order to do this pure hydrogen was allowed to pass through benzene at a known rate and a constant temperature, the amount of benzene in the gas being determined.

TABLE V.—*The Action of Heat upon Hydrogen-borne Benzene.*

Percentage of benzene in original gas	5·28	5·28	5·28
Temperature of gas in the decomposing tube	900° C.	1100° C.	1300° C.
Analysis of the gas after heating—			
Unsaturated hydrocarbons	5·00	3·33	2·43
Containing acetylene	0·00	trace	0·083
Saturated hydrocarbons	0·00	2·87	5·02
Hydrogen	95·00	93·80	92·47
Carbon deposited and oil formed in grms. per 100 c.c. of gas—			
Carbon	0·0	trace	0·01
Oil	trace	0·012	0·00

which shows that the diluted benzene breaks down to acetylene, methane, and carbon, and, finally, to carbon and hydrogen.

Taking the experimental data, it seemed to show that the primary reaction on heating ethylene is the splitting up of 3 mols. into acetylene and methane—

$$3C_2H_4 = 2C_2H_2 + 2CH_4,$$

and that the acetylene then polymerises into higher bodies as—

$$3C_2H_2 = C_6H_6,$$

and that these compounds, by further polymerisation and interactions amongst themselves, of the kind studied by Berthelot and Carnelley (*Chem. Soc. Journ.*, xxxvii., 701), give rise to a large number of others. As the temperature

* A Paper read before the Royal Society.

rises, the methane formed in the primary action splits up into acetylene and hydrogen—

$$2CH_4 = C_2H_2 + 3H_2;$$

and when the temperature has reached the decomposing point of the acetylene, which varies with the degree of dilution, polymerisation takes place no longer, but the acetylene splits up directly into carbon and hydrogen, and all the products formed at lower temperatures doing the same thing, the final reaction is—

$$C_2H_4 = C_2 + 2H_2.$$

An attempt was now made to see how far analytical results would quantitatively bear out the inferences deduced from the foregoing experiments.

To do this, the method adopted was as follows:—The whole apparatus was filled with ethylene. The platinum tube and condensing tube were weighed, and the amount of ethylene in the gas holder measured. The platinum tube was heated to the required temperature, and the gas aspirated through it at a uniform rate of 4·2 c.c. per minute. When sufficient gas had passed through (about 250 c.c.) the stopcocks were turned off, and the amount of gas left in the holder measured. The amount of water displaced from the aspirator was also measured, and in this manner the change in volume was determined. The tube was again weighed, and the gain in weight noted. The platinum tube was also weighed, and then slowly heated to dull redness in a stream of hydrogen, in order to drive off any oil that might have been condensed in it, and again weighed. The tube was now heated to bright redness in a stream of oxygen, in order to burn off carbon, and again weighed. The sample tube was closed, and the contents analysed; the acetylene in the absorption bottles was also determined in the usual way.

Ethylene was first heated to 700—800° C., but no acetylene was formed, no alteration in volume took place, and the gas seemed unacted upon.

The temperature was then raised to 800—900° C., and the following results obtained.

Oil	0·0131 grm. per 100 c.c. gas.
Heavy oil	0·0055 „ „
Carbon	Nil
Decrease in vol...	100 to 89
Acetylene formed	0·057 per cent

On analysis the gas gave—

1. Acetylene	0·06	
Unsaturated hydrocarbons ..	81·38	
Paraffins	6·66	15·83
Marsh gas	9·17	
Hydrogen	0·00	
Nitrogen	3·10	
	100·37	

Original gas—

Ethylene	98·03
Nitrogen	1·97
	100·00

Analysis without paraffin absorption—

2. Acetylene	0·06
Unsaturated hydrocarbons ..	81·25
Saturated hydrocarbons	17·70
Hydrogen	0·00
Nitrogen	3·10
	102·11

0·0186 grm. of oil = 17·3 c.c. of acetylene at 17° C. and 760 m.m. 100 vols. of gas after heating condense to 89 vols. gas and 15·4 vols. acetylene.

Calculating the analysis from a percentage to a basis of 89, we get—

Acetylene	0·05
Unsaturated hydrocarbons ..	72·41
Saturated hydrocarbons	14·00
Hydrogen	0·00
Nitrogen	2·76
	89·22

Taking 72·41 from 98·03 = 25·62 of ethylene decomposed, and, according to the equation—

$$3C_2H_4 = 2C_2H_2 + 2CH_4,$$

25·62 should give—

Calculated 17 vols. of acetylene and 17 vols. of methane
Found .. 15·4 „ „ 14 „ „

the discrepancy in the figures being due to interactions between the products of decomposition, and the result would certainly seem to point to the above equation as representing the initial decomposition.

The next temperature tried was 900—1000° C., and the following figures were obtained:—

Rate of flow ..	4·2 c.c. of gas per minute.
Oil	0·0213 grm. per 100 c.c. gas.
Heavy oil	0·0080 „ „
Carbon..	0·0363 „ „
Decrease in vol...	100 to 98·6.

On analysis the gas gave—

1. Acetylene	1·19	
Unsaturated hydrocarbons ..	15·21	
Paraffins	12·70	40·48
Methane	27·78	
Hydrogen	41·30	
Nitrogen	1·82	
	100·00	

No paraffin absorption—

2. Acetylene	1·19
Unsaturated hydrocarbons ..	15·43
Saturated hydrocarbons	40·77
Hydrogen	40·79
Nitrogen	1·82
	100·00

Explosion of the whole—

Carbon dioxide	73·73 per cent
„ „ calc. from 1 ..	73·28 „
„ „ „ 2 ..	73·96 „

0·0363 grm. of carbon = 36·3 c.c. of acetylene at 19° C. and 762 m.m.

0·0293 grm. of oil = 27·0 c.c. of acetylene at 19° C. and 762 m.m.

Calculating these from 100 c.c. of gas to 98·6 c.c. of gas, we get—

Oil = 26·8 c.c. of acetylene at 19° C.
Carbon = 35·8 c.c. „ „

And calculating the gas analysis in the same manner as before, we obtain:—

Acetylene	1·17
Unsaturated hydrocarbons ..	15·00
Saturated hydrocarbons	39·90
Hydrogen	40·72
Nitrogen	1·81
	98·60

Then the amount of ethylene decomposed is 98·03 − 15·00 = 83·03, and this should give—

$3C_2H_4 = 2C_2H_2 + 2CH_4.$

83·03	55·35	55·35 calculated.
	62·6	39·9 found.

Evidently, therefore, some of the methane has decomposed, forming acetylene and hydrogen. Amount of methane decomposed 55·35 − 39·9 = 15·45—

$$2CH_4 = C_2H_2 + 3H_2.$$
$$15{\cdot}45 \quad 7{\cdot}72 \quad 23{\cdot}16$$

Adding this acetylene on to that already calculated for the decomposition of ethylene, we get 55·35 + 7·72 = 63·07, a figure nearly equal to the acetylene found.

Taking into consideration the complexity of the changes involved and the difficulty in obtaining great accuracy in gas analysis, these results seem to me to prove that the primary action of heat upon ethylene may be represented by the equation—

$$3C_2H_4 = 2C_2H_2 + 2CH_4,$$

whilst the final decomposition is as represested by previous observers—

$$C_2H_4 = C_2 + 2H_2,$$

and that between these two extremes there occur a large number of interactions due to the polymerisation of the acetylene formed from the ethylene, and also at higher temperatures from the methane, according to the equation—

$$2CH_4 = C_2H_2 + 3H_2.$$

In conclusion, I desire to acknowledge my indebtedness to Mr. F. B. Grundy for the assistance he has rendered me in this investigation.

THE ARRANGEMENT OF THE SPECIFIC GRAVITIES OF THE ELEMENTS ON THE PERIODIC SYSTEM.

By U. ALVISI.

ACCORDING to the author, in the periodic system of the elements the following functions are manifested :—

1. With the increasing atomic weight the equivalent of the elements referred to oxygen falls in the limit forms of the oxygen compounds.

2. The specific gravity rises up to a certain point and then descends.

From a comparison of both these functions the author infers :—

The relations between the specific gravities of those elements which in the large periods are grouped symmetrically around the central element show in the first part of the period a movement inversely proportional, and in the second part one directly proportional to the relations between the equiv. of the same elements referred to the limit forms of the same elements, *e.g.*,—

i.e., the matter is arranged on both sides of the central element with the same mean density, *e.g.*,—

One Side.

Na	sp. gr.	0·98
Mg	,,	1·74
Al	,,	2·64
Sum	,,	5·32

Other Side.

P	sp. gr.	2·2
S	,,	2·07
Cl	,,	1·3
		5·57

In the large periods on both sides of the eighth group there are on the right and the left each three elements whose joint sp. gr. is the same. Of the three elements of the eighth group, two give, together with the four first of the large period, the same total sp. gr. as the third element with the four last of the large period, *i.e.*, the eighth group has, to a certain extent, the function of equilibrating the less dense matter of the first part of the large period with the sp. gr. of the second part.—*R. Acc. dei. Lincei* and *Beiblätter der Annalen.*

ELECTROTROPISM AND KINDRED PHENOMENA.

By E. BLASIUS and F. SWEIZER.

THE authors have collected numerous observations upon a great number of animals permanently or occasionally inhabiting water, concerning the phenomena of electrotropism, *i.e.*, the property of certain animals living in water to be affected in their position and in the direction of their movements by a constant electric current. They consider their experiments—in which they had the exceptional opportunity of working with the mighty current of the Berlin Electrical Works at a tension of about 108 volts—as by no means concluded. They hold that a satisfactory explanation of the galvanotropic phenomena in animals is not yet possible, though they venture to submit a (provisional) hypothesis. They mention, as the most striking phenomena observed, especially in fishes: the descending current (the head of the subject being directed towards the anode) occasions calmness or even stupefaction (galvanonarcosis), whilst the ascending current (the opposite position of the fish) produces excite-

First Large Period.

Elements	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co
Equivalents	78	40	29·3	24	28·4	17·3	15·7		
Specific gravities	0·87	1·6	(3·8)	(5·1)	5·5	6·5	7·5	7·8	8·6
Elements	Ni	Cu	Zn	Ga	Ge	As	Se	Be	
Equivalents		126	65	46·6	36	30·7	26·3	22·8	
Specific gravities	8·7	8·8	7·1	5·96	5·47	5·7	4·8	3·1	

Relations of specific gravities of equivalents	Mn/K	Cr/Ca	V/Sc	Cu/Br	Zn/Se	Ga/As
	8·62	4·06	2·2	2·83	1·47	1·04
	1/496	1/2·31	1/1·43	5·57	2·47	1·55

8·62/4·06 = 2·12	4·06/2·2 = 1·84	2·83/1·47 = 1·92	1·47/1·04 = 1·41
4·96/2·31 = 2·14	2·31/1·43 = 1·61	5·53/2·47 = 2·23	2·47/1·55 = 1·59
Diff. = 0·02	Diff. = 0·23	Diff. = 0·31	Diff. = 0·18

In the second small period the sum of the specific gravities of the elements on one side of the central element is equal to the corresponding sum of the other side,

ment up to tetanus. It seems that electrotropism may be conceived as a sum of the movements of the subject which, induced by the sensible excitement of the current,

show the more or less conscious effort of the subject to escape the stimulating effect of the ascending current, and to participate in the tranquillising action of the descending current. The phenomena of electrotropism would consequently proceed from the effect of the current upon the animals' nerves of sensation, and these would ensue, according to Pflüger's well-known law of electrotonus, decrease of excitability at the positive and increase at the negative pole. The authors conceive of the animal as if resolved into two parts, so that it, *e.g.*, if turned towards the anode, is divided into an anterior anelectrotonic and a posterior kataelectrotonic part. In this case the excitability of the brain and of the spinal marrow is educed, and in the opposite it is heightened.

Among single phenomena connected with electrotropism we may mention that fishes, if transversely traversed by the current, display a behaviour analogous to the known symptoms of dizziness (which occur in man on transverse galvanisation of the head), as they always sank on the side turned towards the anode.

The authors made exclusive use of the current of a dynamo machine, but they ascertained by comparative work with an accumulator current at 77·6 volts. that the former current was exactly like a constant current in its effects.—*Pflüger's Archiv.*

THE SEPARATION OF COBALT AND NICKEL.*

By H HERRENSCHMIDT and E. CAPELLE.

(Continued from p. 112.)

According to Baubigny (*Comptes Rendus*) all the zinc is precipitated from a neutral solution of zinc chloride or sulphate at common temperatures by means of sulphuretted hydrogen, provided the solution is sufficiently dilute (0·3 grm. salt to 100 c.c.), and the precipitate is allowed to stand for some hours in closed vessels. For an equal volume of liquid the precipitate must stand so much the longer the greater the quantity of zinc present. In a solution of zinc sulphate containing free sulphuric acid, sulphuretted hydrogen at common temperatures occasions a slight precipitate after some time, and increases gradually. Larger quantities of free sulphuric acid totally prevent the precipitation. If, on the contrary, a solution of zinc sulphate, acidulated with sulphuric acid, is treated with sulphuretted hydrogen in heat, there ensues a more or less complete deposition of the zinc, according to the respective quantities of the zinc salt used and the free acid present, as well as the total volume of the liquid.

If we mix a neutral solution of zinc with acetic acid it behaves, on treatment with sulphuretted hydrogen, exactly like a neutral solution of zinc. Zinc is completely precipitated even from solutions containing from 20 to 25 per cent of acetic acid.

Upon this behaviour of zinc and the different behaviour of the salts of nickel and cobalt under the same conditions, Baubigny founds a method for separating zinc from nickel. This method at the same time allows of the separation of zinc from aluminium, chrome, manganese, and iron (*Comptes Rendus*, cviii., p. 236).

For separating zinc from nickel, the salts of both metals are dissolved in acetic acid at 10 per cent in such proportions that 100 c.c. of the liquid may contain about 0·3 grm. of the salts. The acetic solution is treated with sulphuretted hydrogen at the common temperature and allowed to stand for from two to three hours. The pure white precipitate of zinc sulphide is filtered, and washed with sulphuretted hydrogen water containing 10 per cent of acetic acid. In the filtrate, the nickel is separated in the ordinary manner by adding ammonium acetate, treating with sulphuretted hydrogen at from 70° to 75°, and allowing it to cool in closed vessels in contact with sulphuretted hydrogen. The nickel sulphide is washed with sulphuretted hydrogen water containing from 1 to 2 per cent of acetic acid. The precipitated sulphides are converted into sulphates, heated to about 400° and weighed.

This method yields satisfactory results. If the quantity of nickel present is slight, or amounts at most to one-third part of the zinc, the separation of the sulphates may be effected in a pure watery solution.

The method is inapplicable in presence of considerable quantities of ferric salts.

The separation of zinc from cobalt is practicable only if very little cobalt is present in proportion to the zinc. Hence, Baubigny attempted the separation of both metals in presence of a certain quantity of free sulphuric acid, approximately equal to that existing in combination in the salts. He diluted the solution so as to obtain a complete separation of the zinc; but this method yielded useful results only if the proportion of cobalt was relatively small. An approximate separation was also obtained if only a very small quantity of zinc was present. In order to effect a complete separation under other circumstances, either the quantity of free sulphuric acid must be increased and the liquid correspondingly diluted, or the zinc precipitate, after conversion into sulphate, must again be treated with sulphuretted hydrogen.

According to Baubigny, the separation of zinc from cobalt and nickel may also be effected in the dry way if the chlorides of the metals are heated to the temperature of boiling sulphur. The zinc chloride is completely volatilised, whilst the nickel and cobalt chlorides remain unaffected.

Carnot has determined, by a series of experiments, in what stage of oxidation cobalt and nickel are obtained when they are treated with different oxidising agents in alkaline solutions. These experiments are the more interesting as the methods proposed by E. Fleischer, E. Donath, and Jos. Mayerhofer for the determination and separation of cobalt and nickel presuppose an accurate knowledge of the state of oxidation of the metals. C. Krauss has also occupied himself with the same subject, and his results are confirmed by Carnot's experiments.

The nickel oxide obtained by oxidation with chloride of soda and with bromine in an alkaline solution corresponds exactly with the formula Ni_2O_3.

The cobalt oxide obtained by the use of chloride of soda, bromine, or iodine always contains more oxygen than that belonging to the sesquioxide. The composition of the precipitate with chloride of soda agreed on an average with the formula $Co_{10}O_{16}$, or $2CoO_2{,}4Co_2O_3$, and on precipitation with bromine or iodine it agreed with the formula $Co_{10}O_{16\cdot25}$, or $Co_8O_{10} = 2CoO_2{,}3Co_2O_3$.

A cobalt oxide of the composition Co_2O_3 is readily obtained if a solution of cobalt is boiled with potassa-lye and hydrogen peroxide. Nickel under the same conditions is separated as nickelous hydroxide.

(To be continued).

* *Zeitschrift Analytische Chemie.*

Dr. Arthur W. Bishop, late Assistant Professor at the Heriot-Watt College, Edinburgh, has been appointed by the Secretary of State for India Professor of Chemistry in his Highness the Maharajah of Travancore's College at Trivandrum.

Giles's Modified Litre Flask.—The extreme delicacy of most of the reactions used in volumetric analysis by standard solutions renders it of importance to know the exact strength of the solutions employed. To simplify this standardising, Mr. Giles's modified litre flask, described in a recent issue, has been found of great utility. By its use we have, after the preliminary test, exactly 1 litre of solution to work with, and the calculation of how much water or salt employed has to be added is made very much easier, and in a busy laboratory the saving of time thereby effected is of great importance.

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

SECOND PAPER: THE ANALYSIS OF BARIC CHLORIDE.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 112.)

Experiment 20.—Very pure baric chloride, which had been prepared by many successive precipitations from aqueous solution by hydrochloric acid and alcohol (Sample I.*c*), was coarsely powdered and gradually heated to bright redness by means of a Berzelius spirit lamp in a double platinum crucible. In order to prevent as much as possible the decomposition of the salt, the long-continued ignition was conducted in a stream of pure nitrogen. A large part of the salt was fused during the process. After having been cooled for eight hours over phosphoric oxide in a desiccator, the tightly-covered inner crucible was rapidly weighed, and the weight of baric chloride was found to be 6·36793 grms. in the air. Since the atmospheric pressure and temperature at the time of weighing were respectively 76 c.m. and 20°, the salt would have weighed 6·36900 grms. in a vacuum. The solution of the baric chloride in pure boiled water in a large platinum dish was perfectly clear, and the crucible itself was found to have lost only 0·02 m.grm. in weight. The clear liquid upon being titrated at once with standard hydrochloric acid (see *ante*, p. 92) was found to require 3·40 c.c. of the solution in order to remove the colour of the trace of phenolphthalein added, and 0·64 c.c. more to reach the point at which methyl orange began to show an excess of acid. An excess of yet 0·26 c.c. was added in order to be certain of the end-point. According to previous remarks (p. 65), the correction to be added to the weight of the baric chloride corresponding to the first addition of acid was 0·71 m.grm., while the correction corresponding to the second addition was 0·03 m.grm. Hence, the true weight of the baric chloride in vacuum, if none had been decomposed by heat, would have been 6·36974.

The solution was transferred with the greatest care to a glass-stoppered Erlenmeyer flask, and diluted to about 150 c.c. with cold water. To it was then gradually added in the dark room the cold solution of about 6·72 grms. of silver (about $\frac{1}{15}$ excess). The metal had been dissolved in 13 c.c. of the purest nitric acid, the lower oxides of nitrogen had been expelled, and the whole had been expelled, and the whole had been diluted to over 600 c.c.

The precipitate was shaken occasionally with the liquid for several days in perfect darkness, and the filtrate, which could contain no trace of chlorine, was separated by means of the indispensable Gooch crucible. After having been passed several times through the crucible, in order to avoid the loss of any shreds of asbestos, the filtrate was set aside. The precipitate was violently agitated with renewed portions of cold water until the wash-water was absolutely neutral, and was then transferred to the crucible by means of a jet of water. The last particles of argentic chloride were removed by shaking the stoppered flask violently with a little water. Subsequent testing with ammonia and nitric acid showed that no argentic chloride remained in the flask. The 1300 c.c. of wash-water were evaporated, and the small amount of resulting argentic chloride was collected upon a small washed filter of the best quality. After the rapid ignition of the filter-paper in a porcelain dish, the ash was found to contain 0·70 m.grm. of silver, according to Volhard's method. Hence, 0·93 m.grm. of argentic chloride had been dissolved. The main mass of the precipitate was dried at 180°, and after having been carefully weighed it was transferred to a porcelain crucible, weighed again, fused in an air-bath, and weighed yet again. It is needless to say that organic matter was carefully excluded during all the operations, but nevertheless the argentic chloride was not absolutely colourless after fusion. Perhaps the trace of phenolphthalein and methyl orange may have caused a slight decomposition. It will be seen how the introduction of these indicators was avoided before the close of the investigation.

The final corrected weight of the argentic chloride was found as follows:—

	Grms.
Weight in air of AgCl in Gooch crucible ..	= 8·76657
Correction to vacuum (T° = 22°, H = 76 c.m.)	= +0·00062
Weight in vacuum of AgCl in Gooch crucible	= 8·76719
Loss on fusion in porcelain crucible	= −0·00050
Weight of main mass of fused AgCl	= 8·76669
Weight of AgCl found in wash-water	= +0·00093
Total argentic chloride	= 8·76762
Corresponding to 0·26 c.c. standard HCl added in titration	= −0·00035
Corrected weight of argentic chloride in vacuum	= 8·76727

Since it seemed hardly probable that either of the chlorides was in this case weighed more accurately than within 0·1 m.grm., the fifth place of decimals is omitted below. This practice was always adhered to unless the fifth place seemed to have some significance.

Experiment 20 then leads us to conclude that the ratio of argentic chloride to baric chloride is 8·7673 : 6·3697 = 100·000 : 72·653. Hence, the atomic weight of barium is easily found to be 137·435, a result which agrees almost exactly with that obtained from baric bromide.

(To be continued.)

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences.*

Chair of Chemistry, Royal College of Science.—The Government has decided to place the direction of the Customs and Inland Revenue Laboratories under one administrative chief, to be styled the Principal Chemist of the Government Laboratories. The Principal Chemist will also receive references from the Board of Agriculture, the Local Government Board, and other Government Departments. The appointment, which is in the gift of the Treasury, has been offered to, and has been accepted by, Professor Thorpe, F.R.S., who thereby vacates the Chair of Chemistry in the Royal College of Science, which he has held since 1885.

Isomerism of the Nitrobenzoic Acids.—Oechsner de Coninck.—The ortho- and meta-isomers are easily soluble in water and dilute alcohol, but the para-isomer is very sparingly soluble. In ether the similarity is of the same order; in chloroform and benzene the distinction is less well marked. In light ligroine and carbon disulphide the meta-compound is the most soluble, whilst the ortho- and para-compounds approach each other by their total or almost total insolubility.—*Comptes Rendus*, cxviii., No. 9.

Analysis of a Decayed Cheese; Extraction of a New Ptomaine.—C. Lepierre.—The author has examined a large cheese prepared from sheeps' milk which had occasioned severe digestive troubles in persons who had partaken of it. It was found free from mineral poisons. The albumens and the albumoses gave negative results in experiments upon guinea-pigs. From the group of bases precipitated by cold copper acetate the author obtains a well-crystallised base corresponding to the formula $C_{16}H_{24}N_2O_4$. It was inodorous, bitter, slightly acid to phthalein, sparingly soluble in water, soluble in alcohol. It crystallises in large needles; its chloroplatinate and chloraurate are also crystalline. Its specific rotatory power $(\alpha)_D = +11·3°$ in water. Its salts precipitate with acid sodium phosphomolybdate, picric acid, iodised potassium iodide, but with tannin.—*Comptes Rendus*, cxviii., No. 9.

NEW FORMS OF APPARATUS FOR ORGANIC ANALYSIS.

By Dr. JAMES LEICESTER, F.C.S.,
Lecturer on Chemistry and Metallurgy, Merchant Venturers' Technical School, Bristol.

I BEG to draw the attention of chemists to the following forms of apparatus which were made for me by Herr Hildebrand, of Erlangen, when working in the research laboratory of Professor Otto Fischer in 1888. I have used them in my research work during the past six years, and have found them a help in many ways.

The tube is filled in the usual way with a little glass wool at the top and has the form as shown in B, Fig. 2.

The long limbs are then sealed in the blowpipe, as shown in the lower figure.

A little piece of tubing passes into the bulb, as shown at A, and prevents most of the water from coming into contact with the calcium chloride. The whole apparatus is obviously air-tight.

The form of glass wash-bottle, as shown in Fig. 3, is useful in the case of substances that would act upon cork or indiarubber. It is perfectly air-tight, the gas bubbles through the circle of small holes at the base of A, and the bulb, A, prevents the liquid being drawn back.

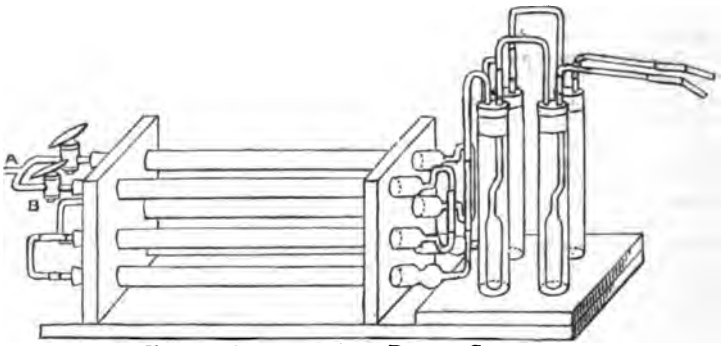

FIG. 1.—APPARATUS FOR DRYING GASES.

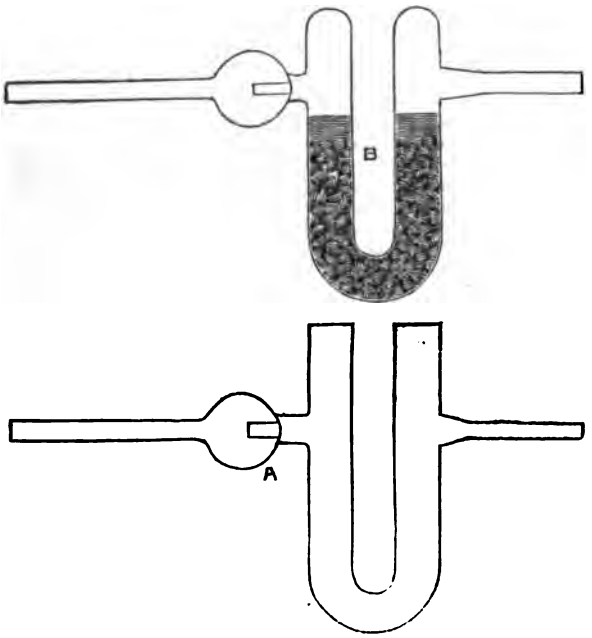

FIG. 2.—NEW CALCIUM CHLORIDE TUBE.

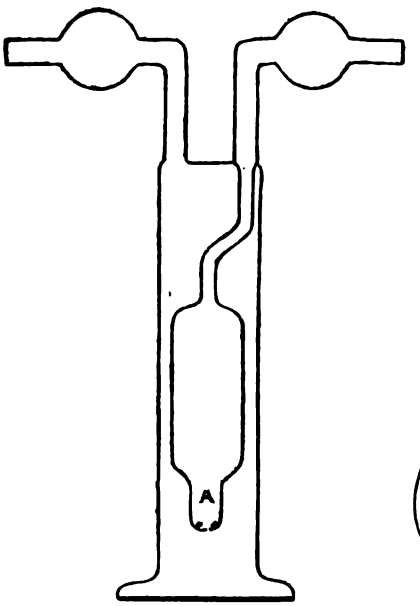

FIG. 3.

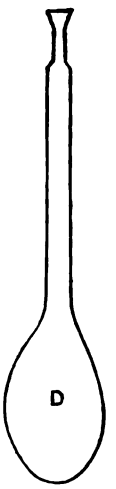

FIG. 4.

The first of the small bottles, Fig. 1, is filled with KHO solution; the second, with H_2SO_4 (conc.). The gas then circulates along the tubes and out at the end marked A. The tubes are filled in the usual way with KHO and $CaCl_2$. Glass wool being placed near to the corks.

One side of the apparatus is connected to an air cylinder, and the other to a cylinder of oxygen, the taps at B regulating which gas is passed through. The whole apparatus is fitted into a wooden stand.

The preparation of ethylene dibromide is conveniently performed in such a way, the bottle being filled with bromine.

Flasks of the form shown in Fig. 4, are very useful to keep the powdered and lump oxide of copper in for analysis. The flasks are strongly heated, and then the ignited oxide of copper poured into them, a copper funnel being used.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 9th, 1894.

Prof. A. W. RÜCKER, M.A., F.R.S., President, in the Chair.

PROF. O. HENRICI, F.R.S., made a communication on "*Mathematical Calculating Machines, especially a New Harmonic Analyser.*"

After mentioning the general principles on which such machines are based, the author showed a new arithmometer, devised by Prof. Selling, in which the jerky motions of the numeral wheels, common in such instruments, are eliminated, and the operations simplified. Another arithmometer, of very compact design, named the "Brunsviga," had been placed on the table by Prof. Boys. The simple and ingenious "Hatchet" integrator was then shown. It resembles a small hatchet with a tracing point projecting at right angles to, and at the end of, the handle. Moving the point from near the centre of mass of any closed curve, round the curve once and back to the starting-point, the distance between the initial and final positions of the hatchet-head is a measure of the area of the curve. The instrument has been found very useful for indicator diagrams.

A Hine and Robertson's planimeter, lent by Prof. Perry, and an Amsler planimeter combined with a pentograph for measuring small areas, an Amsler integrator to give areas and first moments, and a beautiful sphere and cylinder rolling-integrator of great accuracy, by Coradi of Zürich, were shown, as well as an ingenious integraph devised by Abdank Abakonowitcz.

Passing on to Harmonic Analysers, Prof. Henrici explained the objects of such instruments, viz., to determine the coefficients in Fourier's expansion for any periodic curve.

$$y = A_0 + A_1 \cos\theta + A_2 \cos 2\theta + \ldots + B_1 \sin\theta + B_2 \sin 2\theta + \ldots$$

and briefly described Lord Kelvin's instrument, now in use at the Meteorological Office. This machine gives the first term and three pairs of coefficients, A and B, but is large and expensive. The author had endeavoured to devise a simple and more portable instrument, and now described the various stages in the evolution of his new analyser. Using Clifford's method of wrapping the curve round a cylinder, he saw that by imparting a simple harmonic motion to a plane tangential to the cylinder, which plane carried an Amsler planimeter whose tracing-point followed the intersection of the plane with the curve as the cylinder rotated, any coefficient A_n or B_n could be determined. This arrangement had considerable friction, and only gave one coefficient at a time; it also necessitated re-adjustment of the period of the harmonic motion for each pair of terms. Another machine founded on integration by parts was then constructed, in which the relative periods of cylinder and registering wheels was adjusted by a disc and roller, the motion being transmitted to the wheels by bands driven from the disc spindle. This gave A_n and B_n at one operation. Mr. A. Sharp used this machine for some time, and then designed an inversion of it, in which the curve was laid out flat and the machine rolled over it. This arrangement greatly facilitated the multiplication of registering wheels, and thereby enabled several pairs of coefficients to be determined at once. The first machine of this kind showed several small errors, which were avoided in a second instrument—a specimen of which, made by Coradi, was exhibited and described.

A rectangular frame carried on three rollers (two being fixed to the end of a long axis) traverses the paper in the direction of y, and the tracing-point is fixed to a carriage which moves on the frame in a direction perpendicular to y, *i.e.*, in the direction of θ. A band is attached to this carriage and imparts a motion proportional to θ to two longitudinal axes (one for the A coefficients and one for the B's), placed above and parallel to the long roller axis above mentioned. Each of the two axes carries five pinions having teeth in the ratios 1, 2, 3, 4, 5 respectively, which gear with crown wheels fixed to vertical spindles. The latter therefore rotate through angles proportional to θ, 2θ, 3θ, 4θ, and 5θ. To the lower ends of these spindles horizontal rings are attached, in which the bearings of a registering wheel are formed. Each wheel rests on a cylinder carried by the long axis, and rolls or slides thereon, according as its axis be parallel or perpendicular to that of the cylinder. Moving the tracing-point once round the curve gives five pairs of coefficients. By changing the driving band to other pulleys, so as to turn the pinions at different rates relative to the θ movement, the 6th, 8th, 10th, and 7th and 9th pairs can be determined.

The chief drawback of the instrument is that the registering wheels are not easy to read, whilst the backlash of the crown wheels and pinions introduces small errors. In the latest form of instrument toothed wheels are dispensed with, and glass spheres carried in frames on the vertical spindles roll on the horizontal cylinders. Each sphere actuates the registering wheels on fixed axes at right angles to each other, and these respectively give the sine and cosine coefficients. The number of vertical spindles is therefore halved, and the instrument greatly simplified. These details have been introduced by Coradi.

A working drawing of another analyser, designed by Mr. Sharp, which gives the amplitude and epoch of the curve resulting from each pair of terms in Fourier's expansion, was exhibited.

The Discussion on Prof. Henrici's communication was postponed until next meeting.

Mr. H. WILDE, F.R.S., then exhibited and described his "*Magnetarium.*"

This consists of a hollow geographical globe wound all over the inner surface with insulated wire in planes parallel to the equator. Within this globe is a sphere wound with wire on its surface, and having its axis inclined at 23½° to that of the outer pole. By means of epicyclic gearing the spheres can be made to rotate at slightly different rates. When electric currents of suitable strength are passed through the two windings, the magnetic condition of the earth can be imitated, both as regards distribution at any epoch and the secular variations. A better result was obtained by putting sheet iron over the land areas, and a still closer approximation by using thin iron over the water areas. A magnetic chart and tables giving the magnetic elements at various places for different epochs were shown. The author mentioned that recent observations by the United States Survey at Ascension Island, and by Prof. Thorpe in Senegambia, had confirmed results obtained by the magnetarium.

The PRESIDENT said he had tried the apparatus, and found the Siberian oval closely imitated. The secular variations at Greenwich were also well shown. In South America the approximation was not so good.

In reply to a question by Mr. Blakesley, Mr. Wilde said the present position of the pole of the inner sphere was 84° W., 67° N.

Odour of Benzoic Acid. Remarks on Inodorous Substances. — Jacques Passy. — Inodorous substances may be divided into two classes: 1. Those which are for us beyond the limits of perceptibility, *e.g.*, fatty acids beyond the fourteenth term. 2. Those which in the conditions of the experiment are not capable of taking an odoriferous state, *e.g.*, benzoic acid, cinnamic acid.—*Comptes Rendus*, cxviii., No. 9.

NOTICES OF BOOKS.

Our Foreign Competitors, Their Life and Labour. By James Baker, F.R.G.S. London: Sampson Low, Marston, and Co., Ltd. Second Edition.

In these days of keen competition, when we hear so much of the unemployed and the general badness of trade, a book such as the one now before us will be read with much interest. Mr. Baker has had exceptional opportunities of studying the conditions of labour on the Continent, more especially in the few countries which may be called England's principal competitors, viz., Germany, Austria, Belgium, and France.

In a recent speech by one of our foremost politicians it was hinted that if port after port abroad were to be practically closed to English manufactures, by means of prohibitive import duties, England might be induced to retaliate by closing her ports to certain goods of foreign manufacture. These pages, though not written with any such object, may, the author suggests, help some to decide whether such a policy would be beneficial or injurious to English trade. We are inclined to the opinion that the remedy must be found at home, not by taxing foreign goods, but by cheaper production on our own part. Unfortunately for us, the modern tendency, thanks to unrestrained and irresponsible agitators, is all the other way; working men are being constantly urged to "strike" for higher wages and shorter hours, and are so short-sighted as not to see that such a policy must inevitably increase the cost of production and drive the trade away from our shores. Higher wages are only advantageous to a limited number of individuals, and large numbers of others have to suffer for them. Mr. Baker gives some astonishing figures as to the wages earned and the hours worked abroad, thousands of men having to content themselves with 9d. per diem for twelve or more hours' work. Many English capitalists have closed their works at home and started others in foreign countries, simply because of the high wages demanded in England, while the working of the Merchandise Marks Act shows us what a strong foothold foreign competitors have on our shores, our consumption of German manufactures alone having increased by 25 per cent in the last decade. If other nations snatch our foremost position from us we shall have only ourselves to blame; but it is much to be feared that the awakening, when it does come, will be "too late."

Central Experimental Farms, Ottawa; Report of the Chemist. By Frank T. Strutt M.A., F.C.S. 1893.

The seventh annual report of the Chemical Department of the Dominion Experimental Farms gives, in brief outline, arranged for convenience of reference, the data of the work done, and conclusions arrived at which are considered to be of general interest and value to the farming community of the Dominion. This work comprises, amongst other things, the examination of various soils sent from different districts, and reporting on the same, together with such suggestions as to fertilisers and modes of treatment as are deemed advisable for increasing the crop yields. The experiments of the past year have proved that by the treatment herein given in detail the baneful effect of magnesium sulphate in a soil may be overcome. Special attention is called to the value of potash in agriculture, and a plea is made for the better recognition of the value of Canadian wood ashes.

An interesting experiment was made with carrots to determine the difference, if any, in the feeding values between the lower or underground portion and that which was exposed to the light and air. For this purpose white Belgian roots were used, and, on analysing the upper and lower halves, it was found that the former contained a slightly higher proportion of albumenoids and fat than was present in the latter, but not sufficient to make any material difference; but, what is of more importance, it was shown that unpalatable and even poisonous principles are sometimes developed in the exposed portion, but not in the remainder. It is satisfactory to note that the farmers are becoming more particular as to the condition of their water supply; this is a most important subject, especially at a dairy, where a polluted source may spread infection far and wide in an alarmingly short space of time. That the serious attention of the farmers ought to be drawn to this matter is fully shown by the results of 14 analyses of waters from different farms; of this number only five are classed as good or safe for drinking purposes, while the greater number are described as "dangerously contaminated," "seriously polluted," "totally unfit for drinking purposes," "very bad water," and such like.

Institutions of this class are yearly becoming of more and more value in the ever increasing "struggle for existence," and cultivators are recognising, at last, that agriculture, to be successful, must not be carried on merely by rule of thumb, but that great assistance can be rendered by the once scoffed at chemist.

The Australian Farm and House. Melbourne: Tytherleigh and Bayne.

The January number of this publication contains, among other matter, an account of the result of a long series of experiments on the preservation of milk, by Messrs. H. W. Potts and C. C. Lance. These gentlemen some time ago suggested the use of boric acid for this purpose, and, though the useful results then anticipated have been fully borne out, they were, nevertheless, always on the look out for some germicide that would, if possible, give even better results. In consequence of the researches of Professor Koch and other distinguished *savants*, several new antiseptics have been introduced; among them is one named "Formalin," a preparation containing 40 per cent of formic aldehyd. The result of their experiments has been to show that formalin is "an ideal harmless germicide," and has revealed a power of preserving milk quite surprising and far superior to any previously known substance. It is stated that milk has been kept in perfect condition for over a month in the trying heat of an Australian summer, and under severe practical conditions imposed by the creamery managers.

Other experiments in breeding and crossing for increasing the yield of butter have also been carried out by Mr. Potts with excellent results, which will, no doubt, be of great interest to the farmers by whom they will be read.

Appareils et Instruments à l'usage des Physiologistes, Construits d'après les Dessins de M. Léon Marokhovetz. Moscow: T. N. Kouchnerev and Co. Part I.

This pamphlet comprises the description of some of the various apparatus and instruments which were shown at the International Zoological Exhibition held at Moscow in 1892. They are for the most part specially designed for particular work in physiology, and are hardly of much interest to the general reader. A series of twenty-four excellent photographs give much additional clearness to the description in the letterpress.

Le Laboratoire de Physiologie de l'Université Impériale de Moscou. Par M. le Dr. B. N. Popov. Moscow: T. N. Kouchnerev and Co.

The history of the Institute of Physiology connected with the University of Moscow dates from the decree of 1862, when Professor P. Einbrodt was selected to fill the chair. It was he who laid the foundations of the laboratory, and inaugurated the now valuable library. Since his premature death in 1864, the Institute has, in turn, passed under the direction of several others, who have each left behind them a record of some addition

or improvement. Besides the laboratories proper, there is a mechanical workshop, and a lecture hall capable of seating 300 persons. A long list of studies and researches which have been carried on by the different professors and students is given, but as nothing beyond the titles is mentioned, we can form no opinion as to the value of the work done.

CORRESPONDENCE.

THE THEORY OF LE BEL.—A POPULAR ERROR.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS (vol. lxix., p. 2) occurs this statement concerning van 't Hoff and Le Bel:—

"Thus these chemists predicted that all substances which contain an asymmetric carbon atom must be capable of existing in two forms, . . . whilst conversely that *all substances exhibiting optical activity must contain at least one asymmetric carbon atom.*"

That this statement is made by a distinguished follower of van 't Hoff and Le Bel renders its refutation the more necessary, and that such refutation has in vain been published before makes its publication in a paper so widely read as the CHEMICAL NEWS the more to be desired.

May I, therefore, be permitted to point out, with regard to the words italicised:—

First, That Le Bel never advocated this doctrine, but the direct opposite.

Secondly, That for years he has laboured to establish the direct opposite.

Thirdly, That he has succeeded in this.

I. In my book, "A Guide to Stereochemistry" (London, Clarence Eiloart, 1893), I have already stated the facts on this subject as briefly as I could, and I therefore ask permission to repeat them in the same words:—

"The usual statement [Victor Meyer (*Ber. der Chem. Ges.*, xxiii., 574), v. Richter ("Organische Chemie," p. 47), Pattison Muir ("Principles of Chemistry," p. 304)] of Le Bel's theory is that he, as well as van 't Hoff, maintained that every substance optically active in solution contains C (an asymmetric carbon atom). What Le Bel (*Bull. Soc. Chim.*, xxii., 338) maintained was that, 'in general, if a substance is derived from our primitive type MA_4 by the substitution of three different atoms or radicles for A_3, its molecule will be asymmetrical and will possess the power of rotation!' . . . Since 'M is a radicle, simple or complex,' it is *not* necessarily a single carbon atom to which the four unlike groups must be attached to cause rotation. This is the reverse of the usual statement."

"Le Bel then gave the case of a tri-substituted methane as only one example of the application of a principle."

Tri-substitution products of ethylene or benzene might or might not prove to be optically inactive, according as the groups attached to C_2 or C_6 were or were not in the same plane. "The asymmetry of the whole molecule, not the asymmetry of the groups attached to any one carbon-atom in it, was the criterion."

II. In 1882, Le Bel (*Bull. Soc. Chim.*, xxxvii., 300) showed that in ethylene derivatives the four radicles attached to carbon occupy only one plane. His theory demanded that he should either do this or find optically active ethylene derivatives. From 1889 to 1891 he sought optical activity among substituted ammonium compounds containing no C.

III. Finally he discovered (*Comptes Rendus*, cxii., 724) in methyl-ethyl-propyl-isobutyl-ammonium chloride,—

$$\left.\begin{matrix}CH_3\\C_2H_5\\C_3H_7\\C_4H_9\end{matrix}\right\}NCl,$$

an optically active compound containing no C.

Now the importance of all this is not merely historical. Surely, next to knowing that a tri-substituted methane has no plane of symmetry, it is important to know that substituted ethylenes and benzenes, and (probably) ammonias have a plane of symmetry, in which lie all the "peripheral" radicles; the "central" carbon or nitrogen atoms being either in this plane or symmetrically disposed about it. With any other arrangement, optical activity would occur among compounds of these three types. Such is the theory—so constantly ignored—due to Le Bel.

As against C, asymmetric carbon and asymmetric pentad nitrogen compounds which possess a three-dimensional arrangement of atoms, we have then N''' compounds which possess only a two-dimensional arrangement, besides $(C_2)^{iv}$ and $(C_6)^{vi}$ compounds in which the radicles attached to carbon certainly occupy one plane, which is possibly that of the "central" carbon atoms also.

We now see why the myth as to Le Bel's theory has so long survived. "In general," said he, "tri-substitution will destroy symmetry." The assumption underlying this was, of course, that in general the four radicles considered would occupy three dimensions. This most natural assumption has been borne out only in the case where M (in M, A_1, A_2, A_3, A_4) is a simple radicle. Had Le Bel been able to produce an optically active substance in which M was a compound radicle, the myth would at once have been exploded. That such a substance has never been found shows that a two-dimensional arrangement of A_1, A_2, &c., is much more common than was to be expected.—I am, &c.,

ARNOLD EILOART.

Post Graduate Medical School, New York,
February 12, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 9, February 26, 1894.

Action of Heat upon the Double Alkaline Nitrites of the Metals of the Platinum Group: Compounds of Ruthenium.—A. Joly and E. Leidie.—The authors have formerly shown (*Comptes Rendus*, cxii., p. 1259) how the use of potassium nitrite enables us to separate some of the metals of the platinum group, and to effect rapidly the qualitative analysis of their alloys. They have established that it is possible to apply the potassium nitrite concurrently with electrolysis for the exact determination of platinum, palladium, and rhodium alloyed among themselves or with other metals. It was possible to foresee that these compounds, rich in oxygen and easily decomposed at low temperatures, render it possible to prepare oxygen compounds difficult to obtain by other methods. They commenced this study with ruthenium, the oxygen compounds of which, between RuO_4 and binoxide RuO_2, have been studied in detail. The authors have examined two ruthenium-potassium nitrites:—1. A very soluble orange-red salt formed in a neutral liquid, $Ru_2(NO_2)_{6,4}NO_2K$. 2. A yellow salt sparingly soluble in water,—

$$Ru_2O(NO_2)_4,8NO_2K.$$

The ruthenium-sodium nitrites have not yet been described. The only salt obtained is—

$$Ru_2(NO_2)_{6,4}NO_2Na + 4H_2O.$$

The orange-yellow dichroïc prisms are klinorhombic prisms very soluble in water. The action of heat has been tried on the potassium and the sodium salts. The former explodes in a vacuum at 360° to 440°, leaving a mixture of nitrogen and nitrogen dioxide. The authors regard Ru_2O_5,H_2O as hyporuthenic acid.

Derivatives of the Series of Oxazines and Eurhodines.—Charles Lauth.—This paper is not suitable for abstraction.

Certain Laboratory Apparatus.—André Bidot.—This paper requires the five accompanying cuts.

MISCELLANEOUS.

The Late R. H. Davies, F.I.C., F.C.S.—We venture to appeal to our readers on behalf of the widow and sons of the late Mr. R. H. Davies, Chemist to the Society of Apothecaries and Public Analyst for Hammersmith, who are left in somewhat straightened circumstances owing to Mr. Davies' inability to insure his life. Subscriptions will be gratefully received by any of the following Members of the Committee or by the Hon. Sec., Mr. Chattaway, Apothecaries Hall, Blackfriars, E.C.:—

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MEETINGS FOR THE WEEK.

Monday, 19th.—Society of Arts, 8. "Indian Railway Extension—its Relation to the Trade of India and of the United Kingdom," by Joseph Walton.
—— Medical, 8.30.
Tuesday, 20th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
Wednesday, 21st.—Meteorological, 8.
—— Geological, 8.
—— Microscopical, 8.
Thursday, 22nd.—Chemical, 8. (Anniversary Meeting). Presidential Address, Election of Officers and Council.

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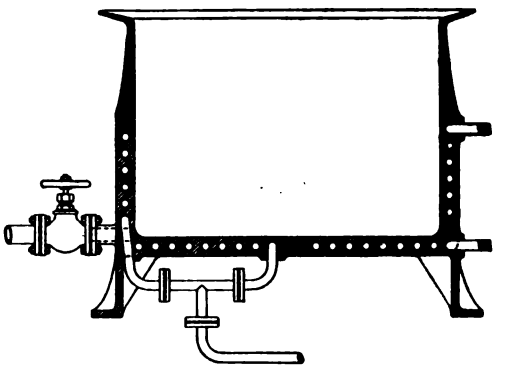

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says;—

P. 316. "An improved vessel for boiling oil, and suitable for many other kindred purposes, has been recently described by T. Frederking (Chemical News, London). A coil of stout piping is arranged in a casting mould, so that the molten metal forming the pan is cast round the coil, much as is done in the case of the water-tuyeres of a blast furnace. Steam at any pressure [or any other heating medium] being passed through the coil, the pan is heated up proportionately without any danger, the pressure bearing solely on the piping and not on the metal pan itself, whilst the well conducting metal walls allow the heat to pass readily. Temperatures up to 350° and 400° C. can be thus obtained."

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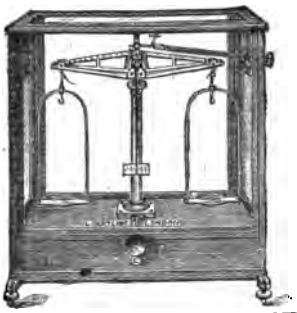

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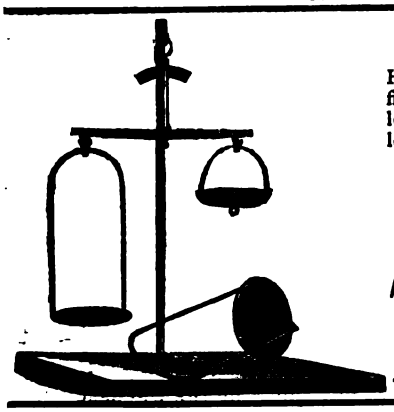

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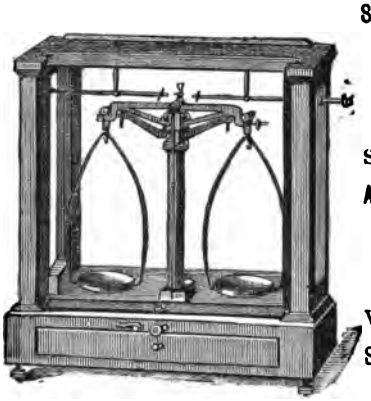

FIG. 3a.

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THE CHEMICAL NEWS.

VOL. LXIX., No. 1791.

ON THE

RELATIONS BETWEEN THE VISCOSITY (INTERNAL FRICTION) OF LIQUIDS AND THEIR CHEMICAL NATURE.*

By T. E. THORPE, D.Sc., F.R.S., and J. W. RODGER, Assoc. R.C.S.

(Concluded from p. 125).

In a second table are given those substances for which the differences exceed this 5 per cent limit. These may be roughly classed as unsaturated hydrocarbons, poly-halogen compounds, formic and acetic acids, benzene, water, and the alcohols.

Similar fundamental constants for molecular viscosity work at the boiling-point have also been deduced. These are given in the following table :—

Fundamental Viscosity Constants (Molecular Viscosity Work at the Boiling-point, in Ergs × 10^8).

Hydrogen	− 1 5
Carbon	50
Hydroxyl oxygen, C—O—H	102
Ether oxygen, C—O—C	27
Carbonyl oxygen, C=O	41
Sulphur, C—S—C	99
Chlorine	109
Bromine (in monobromides)	176
Bromine (in dibromides)	212
Iodine	233
Iso-grouping	5
Double linkage	31
Ring-grouping	60

Tables are also given showing the comparison between the observed and calculated numbers, the substances being classified into two groups, as in the case of molecular viscosity, according as the differences are less or greater than about 5 per cent.

On taking a general survey of the comparisons at the boiling-point, it is evident that for the majority of the substances examined—the paraffins and their mono-halogen derivatives, the sulphides, the ketones, the oxides, and most of the acids and the aromatic hydrocarbons—molecular viscosity and molecular viscosity work may be quantitatively connected with chemical nature. The remaining substances—unsaturated hydrocarbons, di- and poly-halogen compounds, formic acid, benzene, water, and the alcohols—present marked exceptions to the foregoing regularities.

As regards the comparison of the viscosity magnitudes at the corresponding temperature, it is found that, although the critical data are too unsatisfactory to warrant us in laying any particular stress on the relationships obtained under this condition of comparison, these relationships are similar to, even if less definite than, those obtained at the boiling-point. For a property like viscosity, which alters so rapidly with temperature, a corresponding temperature is no better as a condition of comparison than the boiling-point.

On comparing the viscosity curves of those substances which give the best physico-chemical relationships at the boiling-point, it was at once seen that the general shape of the curves towards the boiling-point was practically the same. If tangents were drawn to the curves at points corresponding with the boiling-points of the liquids, the inclinations of the tangents to the axes, that is, the *slopes* of the curves, varied but little. On the other hand, the curves for liquids such as the alcohols, or the lowest members of homologous series, which gave little indication of physico-chemical relationships, had invariably a different shape; the inclinations of tangents drawn at the boiling-point were markedly different from those of the majority of substances. It seemed probable, therefore, that the discrepancies were related to this difference in the value of the slopes, and that, if the temperature of comparison was chosen so as to eliminate this difference, better relationships ought to be obtained. This idea led to the adoption of temperatures of equal slope as comparable temperatures, and, indeed, apart altogether from considerations such as the above, which refer to the particular case of viscosity, much may be said, from a theoretical point of view, in favour of employing such temperatures for physico-chemical comparisons in general.

To begin with, at the temperature of equal slope, the effect of temperature upon the property examined is the same for different substances. In the case of viscosity, for instance, $d\eta/dt$, or the rate at which viscosity is being altered by the temperature, has the same value for all liquids, and this equality might be taken as sufficient justification for supposing that at temperatures of equal slope the substances, so far as viscosity is concerned, are in comparable states.

Another argument which may be advanced in favour of such a method of treatment is that the comparable temperatures are chosen by means of a study of the effect of temperature on the property actually examined. The main objection which can be urged against the boiling-point as a comparable temperature, even when, as in the case of such a property as density, it gives comparatively definite stoichiometric relationships, is that these relationships may not be general. If, however, comparable temperatures be chosen, as in the case of slope by a study of the property considered, the generality of the relationships obtained can be ascertained without the study of other properties of the substances.

Comparisons were made, therefore, at temperatures at which $d\eta/dt$ is the same for the different liquids. Or, graphically, the temperatures may be defined as those corresponding with points on the viscosity curves for which tangents are equally inclined to the axes of co-ordinates. The temperatures are therefore those at which temperature is exercising the same effect on viscosity, and for shortness may be termed *temperatures of equal slope*. The temperatures were obtained by means of Slotte's formula.

It was apparent from the shape of the curves that all the liquids could not be compared at any one value of the slope, because the effect of temperature on the slope varied so much from substance to substance. In some cases—the whole of the alcohols for example—the slope at the boiling-point was considerably greater than that at 0° in the case of some of the less viscous liquids. A slope was, therefore, selected at which as many liquids as possible could be compared. Another slope was then obtained, at which the outstanding liquids could be compared with as many as possible of the liquids used at the original value of the slope. The relationships between the magnitudes of the viscosities of these liquids which could be compared at the two slopes were then found to be the same at either slope, so that general conclusions regarding the behaviour of all the liquids could be deduced. These are as follows :—

1. Temperatures of equal slope tend to reveal much more definite relationships between the values of viscosity coefficients and the chemical nature of the substances than are obtained at the boiling-point.

2. In all homologous series, with the exception of those

* The Bakerian Lecture of the Royal Society.

of the alcohols, acids, and dichlorides, the effect of CH_2 on the value of the coefficient is positive, and tends to diminish as the series is ascended.

3. Of corresponding compounds the one of highest molecular weight has the highest coefficient.

4. Normal propyl compounds have slightly larger coefficients than the corresponding allyl compounds.

5. An iso-compound has invariably a larger coefficient than a normal compound.

6. In the case of other isomers the orientation of the molecule and branching of the atomic chain influence the magnitudes of the coefficients. Similar effects of constitution are also exhibited on comparing saturated and unsaturated hydrocarbons, and the variable effects produced by successive substitution of halogen for hydrogen.

7. The alcohols, and to some extent the acids, still give results which are peculiar when compared with other substances.

As regards molecular viscosity at equal slope the following conclusions may be drawn :—

1. For the great majority of the substances molecular viscosity at equal slope can be calculated from fundamental constants which express, not only the partial effects of the atoms existing in the molecule, but also those due to different atomic arrangements. These are given in the accompanying Table :—

Fundamental Viscosity Constants (*Molecular Viscosity at Slope* $0{\cdot}0_4323$, *in Dynes* $\times 10^6$).

Hydrogen	44·5
Carbon	31
Hydroxyl oxygen, C—O—H	166
Ether oxygen, C—O—C	58
Carbonyl oxygen, C = O	198
Sulphur, C—S—C	246
Chlorine (in monochlorides)	256
Chlorine (in dichlorides)	244
Bromine (in monobromides)	372
Bromine (in dibromides)	361
Iodine	499
Iso-grouping	−21
Double linkage	48
Ring-grouping	244

The large effects which can be attributed to the ring-grouping of atoms, to the iso-linkage, to double linkage, and to changes in the condition of oxygen in its compounds, as well as the smaller effects due to the accumulation of atoms of halogen in a molecule, render evident the quantitative influence of constitution.

2. Of the remaining substances the chlormethanes, tetrachlorethylene, ethylidene chloride, and carbon bisulphide give deviations from the calculated values on account of constitutive influences not allowed for in obtaining the fundamental constants.

3. The alcohols and water exhibit no agreement with the calculated values. The mode in which deviations vary indicates, in the case of the alcohols, that the disturbing factor is related to their chemical nature.

The results obtained from the consideration of molecular viscosity work at equal slope, are of precisely the same nature as those discussed under molecular viscosity.

The fundamental constants are as follows (see Table, next column).

The substances which give deviations from the calculated values fall into two classes. In the first the deviations are to be attributed to chemical constitution, inasmuch as similar disturbing effects may be detected in the magnitudes of other physical properties which afford no evidence of being influenced by molecular complexity.

In the second are substances like the acids, water, and the alcohols, for which the disturbing factor is, no doubt, molecular complexity.

Fundamental Viscosity Constants (*Molecular Viscosity Work at Slope* $0{\cdot}0_4323$, *in Ergs* $\times 10^8$).

Hydrogen	−34
Carbon	148
Hydroxyl oxygen, C—O—H	100
Ether oxygen, C—O—C	43
Carbonyl oxygen, C = O	−19
Sulphur, C—S—C	144
Chlorine (in monochlorides)	89
Chlorine (in dichlorides)	82
Bromine (in monobromides)	151
Bromine (in dibromides)	148
Iodine	218
Iso-grouping	−8
Double linkage	−95
Ring-grouping	−369

The question of the generality of the results obtained is next discussed. It is evident—

1. That over such temperature ranges as the observations extend the results obtained at a particular value of the slope may be regarded as general for all liquids, with the exception of the alcohols, for which the relationships vary slightly as the slope alters. A general expression connecting the viscosity coefficient with the slope is given.

2. It is further indicated, from comparisons made by the use of slopes which varied from liquid to liquid, and which were chosen according to definite systems, that in the present state of the question equal slope is the most suitable condition at which to compare the viscosities of different liquids.

With respect to the relationships existing between the magnitudes of the comparable temperatures of equal slope, it appears—

1. That these vary in a regular way with the chemical nature of the substances, except in the case of liquids like benzene and propylene dibromide, giving viscosity curves which are abnormal when compared with those of their homologues.

2. The temperature relationships may also be regarded as general, and thus independent of the value of the slope, except in the case of the alcohols, which in this respect, as in that of viscosity at equal slope, are anomalous.

The rest of the memoir is concerned with the discussion of certain general conclusions regarding physico-chemical comparisons ; and it finally deals with other possible methods of obtaining and comparing viscosity magnitudes.

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

Second Paper : the Analysis of Baric Chloride.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 129.)

The other analyses were conducted in a similar manner. In some cases, where it was suspected that the wash-water carried with it a trace of finely divided asbestos, the whole quantity was filtered through a washed filter, and the weight found, if appreciable at all, was added to the weight of the Gooch crucible. The Table given below (First Series) is probably comprehensible without further remark, except perhaps the statement that the two figures given in the third column represent the corrections for the baric hydroxide and baric carbonate respectively.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences.*

RATIO OF ARGENTIC AND BARIC CHLORIDES.

First Series.

No. of Expt.	Baric Chloride weighed.	Alk. corr. See p. 65.*	$BaCl_2$ corrected for alkali found.	Argentic Chloride found (fused).	AgCl corresp. to extra HCl.	AgCl in wash water.	Total Argentic Chloride.	Ratio $2AgCl : BaCl_2 = 100 : x$.	At. wt. of Barium.
	Grms.	C.c.	Grms.	Grms.	M.grm.	M.grm.	Grms.		
20	6·3690	3·4 0·6	6·3697	8·7667	0·35	0·93	8·7673	72·653	137·435
21	3·7764	0·3 0·2	3·7765	5·1973	0·20	0·80	5·1979	72·654	137·440
22	3·5846	0·0 0·7	3·5846	4·9332	0·13	1·10	4·9342	72·648	137·423
23	1·5084	0·3 0·3	1·5085	2·0759	0·24	0·86	2·0765	72·646	137·417
24	3·2160	1·1 0·9	3·2163	4·4254	0·64	2·32	4·4271	72·650	137·429
						Average		72·649	137·428

Second Series.

No. of Expt.	Weight of fused Baric Chloride.	Weight of fused Argentic Chloride.	AgCl corresp. to extra HCl.	AgCl in wash water.	Total Argentic Chloride.	Ratio $2AgCl : BaCl_2 = 100 : x$.	At. wt. of Barium.
	Grms.	Grms.	M.grm.	M.grm.	Grms.		
25	1·52384	2·09730	0·00	0·20	2·09750	72·650	137·429
26	5·36010	7·37590	0·10	0·30	7·37610	72·669	137·481
27	3·92244	5·39771	0·12	1·47	5·39906	72·650	137·429
				Average		72·6563	137·446

Third Series.

No. of Expt.	Wt. of cryst. Baric Chloride.	Calc. wt. of Anhydrous $BaCl_2$.	Weight of fused AgCl.	AgCl in wash water.†	Total Argentic Chloride.	Ratio $2AgCl : BaCl_2 = 100 : x$.	At. wt. of Barium.
	Grms.	Grms.	Grms.	M.grms.	Grms.		
28	7·00617	5·97123	8·21488	4·0	8·2189	72·6524	137·435
29	3·85330	3·28410	4·51770	2·2	4·5199	72·6587	137·453
				Average		72·6555	137·444

The weights in the following cases are reduced to the vacuum standard.

The second series of determinations is distinguished from the first by the fact that the baric chloride was fused in an atmosphere of pure dry hydrochloric acid, being contained in a platinum crucible provided with a perforated cover. No phenol-phthalein was added to the salt after its solution, and only a trace of methyl orange, in order to prove its absolute neutrality. Hence, the danger of a slight reduction of silver by compounds of carbon was much lessened. In all other respects the analysis was conducted in a manner similar to that employed in the last series, except that even greater care was used.

The third series differed from the two others in that the baric chloride was not ignited at all. In the two analyses thus made, the true weight of the anhydrous baric chloride taken in each case was calculated from the weight of the homogeneous powdered crystallised salt actually weighed. The determinations of the water of crystallisation previously given (p. 66), which were made at this time, upon this identical sample, showed with great certainty that the percentage of anhydrous salt present must have been 85·2282. Of course, no indicator of any kind was added to the solution before the precipitation. The argentic chloride after having been fused and cooled was of a most beautiful pearly lustre, without a trace of greyness; and in every respect the analyses appeared to be satisfactory.

The discussion of all these results will be found under a later head.

(To be continued.)

* Compare also *Proc. Amer. Acad. Arts and Sciences*, xxviii., 12, also 26.

† Since the excess of silver was very slight, and a portion of the argentic chloride in the filtrate was determined by the evaporation of the strongly acid solution of baric nitrate, it was necessary to apply the correction of +0·0001 grm. previously described (p. 103) to the amount of argentic chloride found in the wash water. The values given above have been thus corrected.

THE QUESTION OF THE OCCURRENCE OF HYDROGEN PEROXIDE IN ATMOSPHERIC AIR AND IN ATMOSPHERIC WATERS.*

By EM. SCHÖNE.

As since 1863 various inquirers (Meissner, Schönbein, H. Struve, Werner Schmid, and Goppelsroeder) have absolutely ascertained the presence of hydrogen peroxide in atmospheric rainfall in single cases at various localities on the earth's surface, I have, in 1874 and 1875, conducted a systematic and extended inquiry in the neighbourhood of Moscow in order to determine the laws to which the quantitative fluctuations of the hydrogen peroxide occurring in the air and in its down-fall are subject.

In 1889, L. Ilosway de N. Iloswa published in the *Bull. Soc. Chim.* ([3], 2, 347, 351, 357, &c.), a series of articles seeking in general to prove that no hydrogen peroxide, and also no ozone, occur in the air and in its downfalls.

He contends that all the reactions from which the presence of these substances has been inferred were due, not to them, but to the nitrous acid present in the air. For the demonstration of the latter he made use of the well-

* *Berichte der Deutschen Chemischen Gesellschaft*, xxvi., p. 3011.

known characteristic and sensitive reaction of Griess with naphthylamine and sulphanilic acid.

(Iloswa maintains that this reagent gives indications in liquids containing one-billionth (!) of nitrous acid. Schöne fixes the limit between the hundred-millionth and the thousand-millionth of nitrous acid).

I confine myself here to a refutation of those assertions of Iloswa's which relate to hydrogen peroxide and its reactions. I shall return in a future treatise to the question of atmospheric ozone.

The arguments which Iloswa advances against the existence of atmospheric hydrogen peroxide are essentially the following:—

I. The reactions with potassium iodide, starch, and ferrous sulphate, as also with tincture of guaiacum and extract of malt, by which hydrogen peroxide is especially shown in the atmosphere, are said not to be characteristic of this substance, but to be also obtained with nitrous acid.

II. The reagents which, according to Iloswa, are exclusively characteristic for hydrogen peroxide, have never shown its presence in atmospheric downfalls.

III. It is said that no chemical processes are known by which hydrogen peroxide and ozone can be formed in nature.

IV. In the process of rapid combustion, ozone is said not to be formed at all, and hydrogen peroxide only under conditions which it cannot encounter in the air.

V. As the chief argument there advanced, the negative result of an experiment made by Iloswa, and which he regards as a kind of *experimentum crucis*. By it he believes that he has definitely proved the absence of hydrogen peroxide and of ozone in the air.

Let us consider these arguments more closely.

1. Potassium iodide—starch—ferrous sulphate is alleged not to be a characteristic reagent for hydrogen peroxide. This allegation is novel. Numerous chemists have used this reagent, by preference, for the demonstration of small quantities of peroxide in the firm conviction that it was perfectly characteristic. If this conviction, based upon careful experimental investigation, is pronounced erroneous, we have the right to expect that the error shall be demonstrated by equally careful experimental researches. But we search in vain for such experiments in Iloswa's memoirs.

He communicates only one experiment, the following:—In a titrated solution of potassium nitrite he liberates the nitrous acid by a few drops of a dilute sulphurous acid at 2 per cent; he adds then potassium iodide, starch, and a few drops of a dilute solution of ferrous sulphate, and finds that by thus proceeding he can as easily detect the "six-millionth part of hydrated nitrous acid with (?) the half-millionth part of hydrogen peroxide." To what end ferrous sulphate was added in this experiment is not intelligible, since it is well known that free nitrous acid *alone*, without the presence of an "exciter," such as ferrous sulphate, sets free iodine from potassium iodide. On the contrary, an addition of ferrous sulphate *decreases* the quantity of the iodine liberated, as it may be easily shown by experiment. Thus *neutral* hydrogen peroxide is distinguished from free nitrous acid, as also from ozone, chlorine, &c., so that at the degrees of dilution here in question there is no *immediate* liberation of iodine from potassium iodide, not until the addition of the "exciter" (ferrous sulphate), and *this difference is a characteristic of hydrogen peroxide.*

As to the sensitiveness of the reaction, Iloswa is of opinion that a smaller proportion than 1 two-millionth (0·5 m.grm. hydrogen peroxide per litre) cannot be recognised. He relies here upon Wilm and Hanriot's "Traite de Chimie" (vol. i., p. 260), which merely repeats a well-known allegation of Schönbein's (*Journ. für. Prakt. Chemie*, lxxix., p. 66, 1860). But the numerical results of the latter are to be received with caution, since quantitative determinations were not his strong side ("Hagenbach, C. F. Schönbein, Basle, 1868, 15). I have repeatedly determined the limit of the sensitiveness of the reaction by exact methods and in presence of numerous persons, who, especially on comparison with a check test, could certainly recognise the colouration produced by this reaction with one twenty-millionth (0·05 m.grm. hydrogen peroxide per litre). Experimentalists well acquainted with this reaction can detect one 25-millionth hydrogen peroxide per litre (0·04 m.grm. per litre); but, of course, only if the test is properly applied. Moreover, Iloswa has—he alleges—observed that old solutions of hydrogen peroxide are more sensitive to potassium iodide, starch, and ferrous sulphate than are recent solutions, since in the former one five-millionth (0·2 m.grm. hydrogen peroxide per litre) were capable of recognition. He explains this, however, by the assumption that such (old) solutions have been rendered more sensitive by the absorption of nitrous acid from the air. This is quite unintelligible, since hydrogen peroxide and nitrous acid react with each other very energetically, forming water and nitric acid, *i.e.*, products which do not intensify the sensitiveness of the solution to the reagent in question, but diminish it.

Even if we were to admit that *free* nitrous acid gives the same reaction with potassium iodide, starch, and ferrous sulphate as does hydrogen peroxide, this fact would in no manner interfere with the detection of the latter in the air and in its downfall. For normal air, at a suitable distance from large cities, industrial centres, volcanos, &c., contains no free acids, as it has been shown in thousands of regular examinations of the atmospheric downfall executed at many experimental stations in Germany, Italy, Belgium (Gembloux, England (Rothamsted), and France (Montsouris), that the nitrogen of the ammonia present in such downfall is, on the average, three times the quantity of that found in the nitrogen acids. The nitrous acids, therefore, in normal air can be present only as *neutral* ammonium nitrite. But Iloswa does not contend that this salt gives the same reaction with potassium iodide, starch, and ferrous sulphate as does hydrogen peroxide.

(To be continued).

THE ACTION OF DRIED AMMONIA ON DRIED CARBON DIOXIDE GAS.

By R. E. HUGHES and FREDK. SODDY.

It has been shown by Baker (*Proc. Chem. Soc.*, 129, 1893) and by Hughes (*Phil. Mag.*, June, 1893) that under suitable conditions the dried gases NH_3 and HCl do not combine. It appeared, therefore, an interesting question to determine whether dried NH_3 and CO_2 combine, as is usually stated in text-books, to form ammonium carbamate. The following experiments were made to elucidate this question, as a result of which we conclude that the above gases when perfectly dry do not combine to form any solid whatsoever. The first method adopted was as follows:—

Carbon dioxide generated by HCl on marble was passed slowly through a series of three Liebig's bulbs containing sulphuric acid, then through a tube about four inches long containing P_2O_5, from whence it passed into a large perfectly dry flask.

The ammonia was produced by the interaction of dry lime and sal-ammoniac. It was dried by being passed through a wide tube about 3½ feet long containing soda-lime previously heated to redness, then through another equally long tube containing solid caustic soda, and finally through a similar tube containing quicklime previously heated to redness. The NH_3 then passed, by means of a second delivery tube, into the dry flask previously mentioned.

The experiment was conducted as follows:—A slow stream of CO_2 was first passed through the apparatus, filling the flask. (It should be mentioned that the flask

was provided with an exit tube connected with a guard tube of soda-lime). Afterwards a slow stream of ammonia was generated and passed through the drying tubes into the flask. A deposit of no great thickness was soon formed on the sides of the clean dried flask. We concluded from this result that much more drying of the reacting bodies must be done before a negative result could be obtained, so the following method of experimenting was substituted:—

Two flasks of about half a litre capacity and provided with side tubes were taken, dried, filled respectively with the CO_2 and NH_3, dried as just described. That containing the ammonia contained some previously-ignited quicklime, and that containing the carbon dioxide contained some pentoxide of phosphorus. When filled these flasks were sealed and allowed to stand for ten days.

The drawn-out ends of the side tubes were connected (before opening) by paraffinned indiarubber tubing provided with a clip. The drawn-out ends were broken off, and the contents allowed to diffuse into one another for twenty-four hours. The very slightest trace of a deposit occurred on the side tube of the flask containing ammonia, but everywhere else the clean surface of the side tubes and flasks was quite undimmed. After diffusion had been allowed to take place as before said for twenty-four hours, a dried current of air was employed to drive out the two gases from the flasks into another dried flask. Not the faintest deposit occurred on the clear interior of this third flask, though the outgoing gases after leaving the last flask smelled strongly of ammonia, and immediately produced a copious precipitate with lime-water.

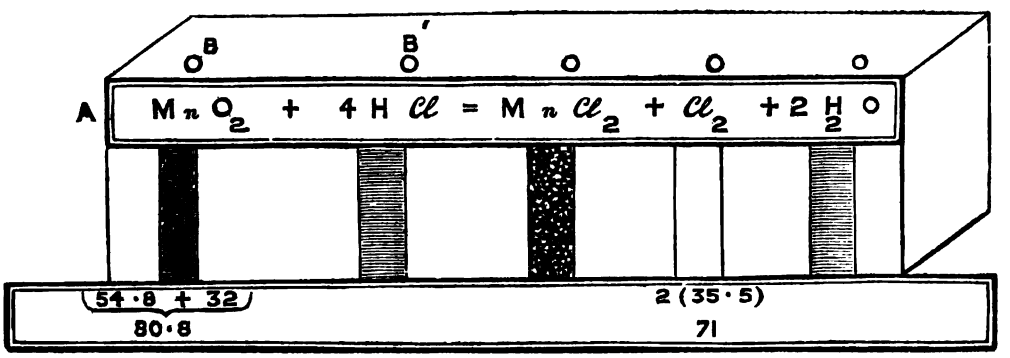
Chemical Laboratory, Eastbourne College,
March 13, 1894.

AN AID TO THE TEACHING OF EQUATIONS.

By Dr. JAMES LEICESTER, F.C.S.,
Lecturer on Chemistry and Metallurgy at the Merchant Venturers' Technical School, Bristol.

I have found the following apparatus of use in teaching equations, chemical problems, and in familiarising my younger students with the appearance of various substances taking part in chemical interactions.

The apparatus is of wood about one yard long. The equations are printed on long cards which run between



grooves at A. Test-tubes filled with the various substances are introduced through the holes in the top marked B B'. At the lower front of the frame is also a grooved space, into which the atomic weights, calculations, &c., can be introduced.

A good exercise is to make the students perform the experiment, separating the products and then filling the tubes with the same.

DETERMINATION OF NICKEL IN NICKEL-STEEL.*

By E. D. CAMPBELL.

The growing importance of nickel-steel has rendered it desirable to have a rapid and accurate method for the determination of nickel in that metal, since the value of the steel is largely dependent upon the amount of nickel which it contains.

The methods in use at present for the determination of comparatively small amounts of nickel in the presence of a large amount of iron, and the separation of the nickel from the manganese and copper, with which it is in most cases associated in this steel, involves usually one or more basic acetate precipitations, and the use of either hydrogen sulphide or of ammonium sulphide in the subsequent work.

On account of the strong tendency of the basic acetate of iron to retain nickel, and of the various objections to the use of hydrogen sulphide or of ammonium sulphide as a precipitant, it was thought desirable, if possible, to devise a method which should not be open to any of the above objections.

The following methods worked out with my assistance by Messrs. Richard Fischer and W. G. Wallace will, I think, be found to be sufficiently accurate for technical work. As the result of a large number of experiments upon solutions of steel, to which had been added known amounts of nickel, manganese, and copper, the last two being added in amounts varying from two to ten times that in which they would occur in nickel-steel, in order that any interference of these elements might be detected, it was found that the nickel could be accurately determined within 0·001 grm., the usual error not exceeding 0·0003 grm. to 0·0005 grm. The amount of nickel recovered is usually a little higher than the true amount, the increase being due to the solubility of ammonium manganous phosphate, the manganese of which accompanies the nickel in the subsequent work. The principles involved in the processes below described are the following:—

1. The iron is precipitated as ferric phosphate in cold strong acetic acid solution, under which conditions it precipitates perfectly free from nickel, although retaining a small amount of copper.

2. The copper is separated from manganese and nickel in hydrochloric acid solution by means of granulated lead.

3. The manganese and lead, which displaced the copper, are separated from the nickel by means of a cold ammoniacal solution of sodium phosphate.

* From the *Journal of the American Chemical Society*, xvi., No. 2.

4. The nickel is determined in the ammoniacal filtrate from the phosphate of manganese and lead, by titration with standard potassium cyanide or by electrolytic deposition.

In case the nickel is accompanied by cobalt, the latter metal remains with the nickel, and may be separated from it by any of the well-known methods after dissolving off the electrolytically deposited nickel.

The two methods described below are identical up to the point where a portion of the filtrate from the phosphates of manganese and lead is taken. The description of that part of the methods common to both will be first given, and then the two ways of treating the above filtrate for the final determination of nickel will be detailed.

Details of Methods.

Take 2·2222 grms. of nickel-steel, place in a 500 c.c. graduated flask, add 20 c.c. nitric acid (sp. gr. 1·20), and 5 c.c. strong hydrochloric acid (sp. gr. 1·21). Boil until the solution is clear, which will usually require not more than from five to ten minutes. Remove from the plate and add 155 c.c. sodium phosphate solution. If a slight precipitate should form which does not dissolve upon shaking, add carefully a few drops of hydrochloric acid until the solution clears up. Add 25 c.c. strong acetic acid (sp. gr. 1·04), then 100 c.c. sodium acetate solution, shake, dilute with water to 502·5 c.c., shake again, and allow to stand fifteen minutes. Filter through a dry 25 c.m. filter, catching the filtrate in a dry beaker. As soon as enough of the filtrate has run through, which requires about ten minutes, draw off with a pipette 250 c.c. of the filtrate, transferring to a No. 4 beaker. This will give one-half of the solution, since it was found by experiment that the ferric phosphate from the amount of steel taken occupies 2·5 c.c. Bring the solution to a boil and add 20 grms. potassium hydroxide previously dissolved in 40 c.c. of water. Boil five minutes, then keep just below boiling point until the precipitate has settled and the solution is clear. This precipitates copper, manganese, and nickel so completely that the filtrate gives no colour with hydrogen sulphide. Filter through asbestos, using a pump, decanting as much of the solution as possible before allowing the precipitate to get upon the filter. Wash with water. Dissolve the precipitate on the filter in a hot solution of 6 c.c. strong hydrochloric acid with an equal volume of water. Wash the filter, using only as much water as is necessary. To the solution in the flask, which should not exceed 50 c.c. and should have a temperature of 40° to 50° C., add 15 grms. granulated lead and agitate at frequent intervals for five to ten minutes. This will completely precipitate the copper, a small amount of lead going into solution. Filter through a small glass-wool filter, catching the filtrate in a No. 2 beaker; wash the granulated lead with a small amount of water, and boil the solution down until it does not exceed 60 c.c. Add 10 c.c. of sodium phosphate solution, then ammonium hydroxide until a precipitate just forms, then hydrochloric acid until the solution just clears up, cool until cold, and transfer to a cylinder or flask graduated to 111·1 c.c. Add 5 c.c. strong ammonium hydroxide (sp. gr. 0·90), dilute to the mark, shake well, and allow to stand fifteen minutes. Filter through a dry 9 c.m. filter, receiving the filtrate into a dry beaker. Draw off, by means of a pipette, 100 c.c. of this filtrate, which is equivalent to 1 grm. of the original steel, and treat by one of the two following methods:—

I.—*Electrolytic Method.*

Transfer the 100 c.c. of filtrate above mentioned to a large platinum dish having a capacity of about 200 c.c. Add 25 c.c. of strong ammonium hydroxide (sp. gr. 0·90), and dilute to 175 c.c. Electrolyse for at least four hours, preferably over night, using a current yielding 4 c.c. of electrolytic gas per minute. This strength of current can be easily obtained by connecting three medium sized cells. A very satisfactory arrangement to avoid the excessive loss of ammonia and the spattering of the solution due to the active evolution of gas, is to cover the platinum dish with a large watch-glass perforated in the centre, through which the positive electrode, consisting of a large platinum cone, is suspended by means of a platinum wire.

The end of the precipitation of the nickel is indicated when a drop of the solution placed upon a drop of ammonium sulphide gives no colour due to nickel sulphide. When the nickel is completely precipitated, disconnect the battery, wash the nickel thoroughly with water, then finally twice with alcohol, and, after draining off as much as possible, heat for a few minutes in an air-bath at 110°. Cool and weigh. After getting the combined weights of the platinum dish and nickel, dissolve off the latter by warming with 5—6 c.c. of nitric acid (sp. gr. 1·20), then wash the platinum dish by means of water and alcohol, and dry and weigh as before. The difference in the two weighings gives the nickel.

It is more satisfactory to weigh the empty dish after the precipitated nickel has been dissolved off than before electrolysis, since in this way a shorter time will elapse between the two weighings, and consequently less error will be introduced from variations in atmospheric conditions. This latter source of error may be still further reduced by employing as a counterpoise for the platinum dish, upon which the nickel is precipitated, a similar platinum dish, washed, dried, and cooled under the same circumstances as the former.

II.—*Volumetric Method.*

Take 100 c.c. of the filtrate from the phosphate of manganese and lead, add hydrochloric acid very carefully until the blue colour of the double ammonium-nickel chloride disappears, then add ammonium hydroxide, drop by drop, until the blue just reappears, and add an excess not exceeding 1 c.c. Dilute to 200 c.c., add 5 c.c. of cupric ferrocyanide indicator, and run in standard potassium cyanide until the solution turns from the purple colour of the indicator to a perfectly clear light straw-yellow. Subtract from the number of c.c. of potassium cyanide used the correction for the indicator. The difference gives the amount necessary to convert the nickel into the double cyanide of potassium and nickel. Multiplying this by the factor of the potassium cyanide, expressed in metallic nickel, gives the amount of nickel in 1 grm. of the original sample.

Special Apparatus and Reagents.

500 c.c. graduated flask with an additional mark at 502·5 c.c. 250 c.c. drop pipette. 100 c.c. drop pipette.

Glass stoppered cylinder or flask graduated to 111·1 c.c. The graduated apparatus should be carefully calibrated and compared before using.

Sodium phosphate solution, made by dissolving 200 grms. of the ordinary crystallised disodium-hydrogen phosphate in 1860 c.c. of water. 10 c.c. of this solution contain 1 grm. of the crystallised salt, and it requires 70 c.c. to precipitate 1 grm. of iron as ferric phosphate.

Sodium acetate solution, made by dissolving 250 grms. crystallised sodium acetate in 820 c.c. of water. 100 c.c. of this solution contain 25 grms. of sodium acetate, which is a slight excess over that which is necessary to convert the nitric and hydrochloric acids to sodium nitrate and chloride, with the liberation of the corresponding amount of acetic acid.

Granulated Lead is of the same quality as that used in assaying. In size it should be that which passes through a sieve with twenty meshes to the inch, but remains upon a sieve with forty meshes.

Before using, the lead should be washed with dilute hydrochloric acid (one part acid to two parts water) in order to dissolve any oxide that may be present.

Standard Nickel Solution.—This may be made from chemically pure nickel by dissolving 2·5 grms. nickel in fifty c.c. nitric acid, sp. gr. 1·20, adding an excess of hy-

drochloric acid, evaporating on a water-bath nearly to dryness, then diluting to 1000 c.c.; 1 c.c. equals 0·0025 grm. nickel. Or it may be made from chemically pure nickelous chloride by dissolving 6 grms. in water with the addition of a few drops of hydrochloric acid, and diluting to 1000 c.c. This latter solution must be standardised. In order to do this, take 30 c.c., place in a large platinum dish, add 25 c.c. of strong ammonium hydroxide, dilute to 175 c.c., and electrolyse as in the electrolytic method for nickel.

Standard Potassium Cyanide Solution.—Take 12 grms. of chemically pure potassium cyanide, dissolve in water, dilute to 1 litre. This must be standardised against a standard nickel solution. Since the presence of ammonium salts interferes somewhat in the titration with potassium cyanide, necessitating the use of a slightly greater amount of potassium cyanide than would be required if there were no ammonium salts present, it is better that the potassium cyanide be standardised under the same conditions as are met in analysis. To standardise the potassium cyanide, take 15—20 c.c. of standard nickel solution, add 6 c.c. of hydrochloric acid, sp. gr. 1·20, 10 c.c. sodium phosphate solution, ammonium hydroxide until the solution turns blue, and then 5 c.c. in excess. Now add hydrochloric acid until the blue colour of the double nickel chloride disappears, then again ammonium hydroxide until the blue just reappears, and an excess not exceeding 1 c.c. Dilute to 200 c.c., add 5 c.c. cupric ferrocyanide indicator, and run in potassium cyanide until the solution changes from the purplish colour imparted by the indicator to a perfectly clear, light, straw-yellow.

Divide the amount of nickel in the standard nickel solution taken by the number of c.c. of potassium cyanide used, less the correction for the indicator. The result will give the strength of the potassium cyanide expressed in metallic nickel.

Cupric Ferrocyanide Indicator.—Take 2·5 grms. of crystallised cupric sulphate, dissolve in 25 c.c. of water, add to this a solution of ammonium oxalate until the precipitate first formed just re-dissolves, then dilute to 500 c.c. Dissolve 2·5 grms. of potassium ferrocyanide in 500 c.c. of water, then slowly pour this solution into the cupric sulphate solution, stirring constantly during the operation. This will give a deep purplish brown solution of cupric ferrocyanide, which may precipitate partially on standing; but the precipitate so formed will be so fine that it will easily remain in suspension for a long time upon shaking the bottle, thus insuring uniform composition. To find the correction for the indicator take 200 c.c. of water, add 6—8 drops of ammonium hydroxide, then 5 c.c. of indicator, taken after shaking the bottle well, and then run in potassium cyanide until the characteristic change of colour is obtained.

Five c.c. of cupric ferrocyanide of the above strength require from 0·15—0·2 c.c. of potassium cyanide, 1 c.c. of which is equivalent to 0·0025 of nickel. If a stronger end reaction is desired, 10 c.c. or even 15 c.c. of the indicator may be used and a suitable correction made.

Repeated analyses of steel have shown that the nickel may be determined by the volumetric method within from 0·0003 to 0·0005 grm. of the true nickel content, duplicate determinations being made in three hours. The electrolytic method requires three hours to the time the solution is ready for electrolysis.

The Atomic Weight of Palladium.—The recent researches of G. H. Bailey and Thornton Lamb (*Journal of the Chemical Society*) find a mean result of 105·459. Keller and Smith (*American Chemical Journal*) give the value = 106·914. Joly and Leidie find the atomic weight of palladium = 105·438. The editors of the *Zeitschrift fur Analytische Chemie* do not accept any of these results as satisfactory.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 28TH, 1894.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, March 8th, 1894.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from February 1st to February 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined 4 were clear but dull, and all the rest clear and bright.

Again we have to record a deficient rainfall, which has only been 1·6 inch at Oxford instead of 2·92 inches, the average of 25 years. It will be remembered that the month of February last year was one of the few months in which the rainfall was in excess of the average.

The tables show a slight change in the Thames-derived waters in respect of the colour and quality of the small proportion of organic matter present. This will be best seen by putting the results of the last few months in a tabular form:—

	Ratio of Brown to Blue tint. Means.			Ratio of Organic Nitrogen to Org. Carbon. Means.		
	Brown.		Blue.	Org. Nit.		Org. Car.
1893, November..	15·5	:	20	30·3	:	100
December..	19·4	:	20	26·6	:	100
1894, January ..	24·2	:	20	24·5	:	100
February ..	23·3	:	20	18·3	:	100
1893, February ..	23·6	:	20	20·3	:	100

With the accumulation of vegetable matter, dead leaves, &c., last autumn, the peaty brown matter in the waters somewhat increased, rising to a maximum in January last, and now again declining. Simultaneously, the organic carbon has increased a little, while the organic nitrogen has remained practically the same. A comparison of the ratios of organic nitrogen to organic carbon, calling the latter 100, is very instructive in connection with the variation in colour. Whilst the ratio of nitrogen to carbon, even in November, was low, showing that the vegetable constituents of the organic matter present were in excess, it is seen that this ratio has been continuously decreasing, until last month it was only as 18·3 to 100, showing a preponderating amount of harmless vegetable matter in the minute quantity of total organic matter present in the waters.

The winter character of the supply has not been strongly marked during any of the recent months, and it even seems as if the high standard of summer purity would soon be reached. A few weeks' sharp frost, with snow and fogs, are, however, not outside the probabilities

of our climate, and with the advent of such wintry conditions a change from the summer to winter quality of the water supply would doubtless take place.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.

THE SEPARATION OF COBALT AND NICKEL.*

By H HERRENSCHMIDT and E. CAPELLE.

(Concluded from p. 128.)

For determining the available oxygen in the precipitated cobalt and nickel hydroxides Carnot mixes the washed precipitate in a flask with solution of potassium iodide in excess, and then with a little dilute hydrochloric acid. After the precipitate has dissolved in the cold, the free iodine is determined with sodium thiosulphate, titrating back the excess of the latter with dilute solution of iodine. Less to be recommended is the determination with ferrous sulphate or oxalic acid and permanganate in a sulphuric solution.

Carnot has attempted to improve Vortmann's method of separation for cobalt and nickel, using as oxidising agents bromine and hydrogen peroxide instead of sodium hypochlorite. In the oxidation with bromine, the solution of the metals containing a sufficiency of ammonium salts or of free acid is mixed in the cold with bromine and supersaturated with ammonia. The hydrogen peroxide may be added either after or before the mixture with ammonia. After oxidation with bromine, the ammoniacal solution turns of a bright rose colour if only cobalt is present; in presence of both metals, there appears a violet colouration. In oxidation with hydrogen peroxide the original brown colour of the solution passes, in the cold, after a few minutes into a purple-red or rose, according as more or less cobalt is present. A rose-violet colouration indicates the presence of a larger quantity of nickel. In heat the change of colour is almost immediate. For the qualitative recognition of cobalt, the solution must be observed in the cold, as the colouration due to cobalt decreases manifestly in heat.

The ammoniacal solution may be heated to 100° and kept at this temperature for some time without the formation of turbidity; but on prolonged heating the liquid becomes turbid, as the cobalt passes from the state of a purpureo-cobaltic salt to that of a luteo-cobaltic salt. From the clear ammoniacal solution a sufficient excess of potassa-lye in the cold throws down the nickel entirely as nickelous hydroxide, and in the filtrate the cobalt may be precipitated by hydrogen sulphide or ammonium sulphide.

In this manner Carnot could not effect a complete separation of cobalt and nickel, and satisfactory results were obtained only when the entire operation had been repeated once or twice. It is most to be recommended to heat the oxidised ammoniacal solution to 100° for a few moments only, to allow it to cool, diluting it with much water, and to precipitate with potassa-lye.

Carnot has obtained various compounds by precipitating the ammonium-cobalt salts, as well as the pure cobalt salts, with ammonium tungstate and ammonium vanadate, and has determined their composition and properties.

For the separation of iron from cobalt and nickel, Le Roy proposes the following procedure:—

Cobalt, nickel, manganese, and iron, the last of which must be present as a ferric salt, are brought into a sulphuric solution. To the liquid is added a minimum of a non-volatile organic acid, preferably citric acid, and a concentrated and very strongly ammoniacal solution of ammonium sulphate is then added in large excess. On the electrolysis of the clear ammoniacal solution (using a current of 300 c.c. detonating gas per hour) the manganese is deposited at the positive pole, and the nickel and cobalt, along with the iron, at the negative pole. After the metals have been entirely eliminated, the current is interrupted, and the negative electrode removed and quickly washed with boiling distilled water. It is then plunged into a concentrated solution of ammonium sulphate supersaturated with ammonia. This electrode is then connected with the positive pole of the battery. The second, or platinode, which will have been weighed, is connected with the negative pole, whilst a current of 100 c.c. detonating gas per hour is introduced. By the action of the current, the metals at the positive electrode oxidised; whilst the oxygen compounds of cobalt and nickel dissolve in the ammoniacal liquid and are then re-deposited in the metallic state upon the negative electrode. The iron is meanwhile converted into insoluble hydroxide, which partly remains on the electrode and partly floats in the liquid. The ferric hydroxide thus obtained contains no trace of cobalt and nickel. These metals are totally eliminated.

L. Mond, C. Langer, and F. Quincke have studied the action of carbon monoxide upon metallic nickel. If carbon monoxide is passed at a temperature of 350° to 450° over metallic nickel in a state of fine division there remains a black carbonaceous mass from which the nickel cannot be entirely extracted by means of an acid. A small quantity of nickel can in this manner oxidise very much carbon monoxide, and there is ultimately formed a substance containing about 85 per cent of carbon and about 15 per cent of nickel. There is also formed a volatile compound of nickel, which is more conveniently obtained by causing dry carbon monoxide to pass over nickel reduced by hydrogen and heated to about 100°, the gas formed being collected in a freezing mixture. It there condenses to a colourless liquid which boils at 43°, and congeals at −25° to a mass of crystalline needles. The formula of this compound is $Ni(CO)_4$. It dissolves in alcohol, more readily in benzene and chloroform. It is not attacked by dilute acids and alkalis. It reduces ammoniacal solutions of silver and copper. At about 180° it is resolved into carbon monoxide and nickel.

In spite of numerous experiments, no analogous compounds have been obtained with cobalt, platinum, iron, and copper. Hence the use of carbon monoxide is recommended for the absolute separation of cobalt and nickel. Mirrors of nickel obtained by heating carbon monoxide nickel contain not a trace of cobalt.

* *Zeitschrift Analytische Chemie.*

THE WIDE-SPREAD OCCURRENCE OF BARIUM AND STRONTIUM IN SILICATE ROCKS.

By W. F. HILLEBRAND.

Among the mass of published analyses of igneous eruptive and metamorphosed eruptive rocks, those in which barium and strontium are noticed are few indeed, unless the work has been of a special nature, like that of Sandberger in the development of the lateral secretion theory. Yet the very numerous analyses of igneous eruptive rocks of all ages and kinds made in the laboratory of the United States Geological Survey during the past thirteen years, have shown that these elements are distributed widely and in considerable quantity, in the United States at least, and doubtless elsewhere.

The percentages of barium and strontium oxides when present are usually below 0·1 per cent each, but higher

amounts are by no means uncommon, and for certain districts seem to be the rule rather than the exception. Within the past year two series of rocks from Colorado and Montana have been analysed, both of which are noteworthy for the high percentages of barium found in them. Of seven rocks constituting the Colorado series, six held from 0·13 to 0·18 per cent BaO, while in the seventh the percentage was 0·43. The SrO ranged from 0·07 to 0·13 per cent for six, and was 0·28 per cent for that one highest in BaO. Of thirteen geologically related rocks from Montana, embracing basic as well as acid and intermediate types, the range of BaO was from 0·19 to 0·37, with an average holding of 0·30 per cent. Three others of the same series contained 0·10 per cent or less, while the seventeenth carried 0·76 per cent BaO. The SrO ranged from 0·37 per cent in the last instance to an average of 0·06 per cent for the other sixteen.

In view of the above showing the question arises, why was not this general distribution sooner recognised? The answer is undoubtedly given by the statement that it has not been the custom among chemists to look for barium and strontium in analyses of the kind under discussion, and doubtless for the following reasons:—

1. A belief on the part of many that the two elements were absent from most rocks, this belief being based on the supposed rarity of the few rock-constituting minerals known to contain barium and strontium as noteworthy constituents.

2. Admitting the possibility of their presence in minute quantities, the unimportance as an aid to classification by the lithologist of the knowledge that a rock may contain a few hundredths of one per cent, more or less, of barium or strontium.

The unsoundness of the first argument has been sufficiently demonstrated by the data given above for rocks of the United States, which show likewise what serious errors may be incurred by neglect to test for the elements in question. Barium- and strontium-carrying minerals, sometimes with high percentages of one or both, are more common rock constituents than was formerly supposed.

With regard to the second point it may be said that if the present decade or the next may be unable to make use of the knowledge referred to, this will probably not hold true of the lithologists of a still later period—an argument perhaps equally applicable to other elements than barium and strontium.

Regarding a further reason why barium has undoubtedly often been overlooked, the reader is referred to another paper, which will appear in our next issue.—*Journal of the American Chemical Society*, xvi., No. 2.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 1st, 1894.

Dr. Armstrong, President, in the Chair.

Messrs. Henry E. Burgess, F. D. Chattaway, Walter Grafton, D. H. Jackson, and A. Lapworth were formally admitted Fellows of the Society.

The list of Officers and Council nominated by the Council for election, at the Anniversary Meeting in March, was read from the Chair.

Certificates were read for the first time in favour of Messrs. Robert William Buttemer, St. Mary's, Godalming; George Hugh Gabb, 91, Elgin Avenue, W.; Matthew A. Parker, 13, Hamilton Crescent, Partick, Glasgow; James Swinburne, 4, Hatherley Road, Kew Gardens.

The following paper was read:—

118. "*The Aërial Oxidation of Terpenes and Essential Oils.*" By C. T. Kingzett.

After referring to his previous work on the subject, the author describes the results of an examination of a number of oily and semi-resinous products obtained on oxidising various turpentines by passing air either into the oil or into a mixture of the oil and water.

It is found that when any terpene is oxidised by air in the presence of water, or when the oxidised oil is shaken up with water, the aqueous solution always contains hydrogen peroxide and a substance that may be obtained by evaporating off the water, this latter at the ordinary temperature of the atmosphere having the consistency of soft pitch, and being very bitter to the taste. Analyses are quoted of a considerable number of samples prepared from various oils, showing that the composition of the substance is approximately represented by the formula $C_{10}H_{16}O_3$. It appears to yield some cymene when distilled with dilute sulphuric acid.

When Russian turpentine is oxidised in the presence of water and the aqueous solution is distilled, a small quantity of a light-yellow coloured oil passes over, which darkens on standing, and has a characteristic smell something like that of thymol. About 23 grms. of this oil were obtained by distilling 25 litres of the fluid. On analysis it gave numbers approximating to those corresponding with the formula $C_{10}H_{14}O$; but on distilling this oil, after drying it over calcium chloride, only a portion passed over between 180° and 205°, leaving a viscid residue.

When oxidised Russian turpentine is evaporated down on the water-bath until all the volatile matter has apparently been driven off, and the residue is dried at 100°, a dark brown translucent mass is obtained, which, when cold, is quite hard and brittle; an analysis of this substance shows that it has a composition represented roughly by the formula $C_{10}H_{14}O_2$. Other oils afford somewhat similar results.

The author believes that in the limited oxidation (by air) of essential oils the terpene grouping is not broken down, as he has ascertained, by special investigation, that the acetic acid which sometimes accompanies the other products when the process is conducted in the presence of water is not observed to be present if only pure or refined oils are employed, and he has not met with any product which can be assumed to contain less than 10 atoms of carbon in the molecule.

The author does not propose to continue the study of these substances, and will be pleased to supply any quantity of the chief products to any chemist who may desire to examine them.

The experiments have been carried out with the assistance of Mr. D. Homfray, B.Sc.

119. "*The Amides of Sodium, Potassium, and Lithium.*" By A. W. Titherley, B.Sc.

Sodamide ($NaNH_2$) was prepared by the action of dry ammonia on sodium heated to 300—400° in a polished iron retort; as obtained in this way, sodamide is a white mass, having a distinctly crystalline structure; the brown colour of the substance prepared by former observers is principally due to organic impurity in the sodium. The product was proved to have the composition represented by the formula $NaNH_2$ by synthethical experiments. When heated at 500—600°, sodamide decomposes into sodium, nitrogen, and hydrogen, but no sodium nitride (Na_3N) is obtained; in fact all attempts to prepare this compound were unsuccessful. The same is true of disodium amide (Na_2NH), which cannot be produced by the action of sodium on sodamide; the metal, however, dissolves in the molten sodamide, forming a blue product, the exact composition of which could not be ascertained.

By acting with ammonia on heated sodium oxide a mixture of sodium hydroxide and sodamide was obtained.

Potassamide (KNH_2) may be obtained as a white solid

by using the same method as that used in preparing sodamide. It is less brittle and softer than sodamide, and it melts at a higher temperature. It is capable of crystallising, and sublimes when heated to about 400°. No potassium nitride (K_3N) could be obtained by heating potassamide, the compound breaking up into potassium, nitrogen, and hydrogen.

Lithamide ($LiNH_2$) may be obtained by the same method as sodamide and potassamide. It is a white crystaline solid. Both sodamide and potassamide decompose silica when heated with it, silicon nitride and sodium silicate apparently being formed. A similar change occurs with boric oxide, boron nitride being one of the products.

Nitrosyl chloride acts on sodamide, forming potassium chloride, nitrogen, and water.

When sodamide is heated with alkylic haloids, ammonia is produced and not the corresponding amine.

CORRESPONDENCE.

THE NESSLER PROCESS IN WATER ANALYSIS.

Monsieur l'Editeur du CHEMICAL NEWS *à Londres.*

Je m'empresse de vous remercier pour la notice que vous consacrez dans votre No. 1789, du 9 de ce mois, à mon "Traité de Chimie analytique."

Je remercie également l'auteur de cette note, d'avoir attiré mon attention sur l'erreur que j'ai commise en attribuant à Messieurs Frankland et Armstrong, le procédé de dosage colorimétrique de l'ammoniaque par le réactif de Nessler. J'ai recherché ce qui avait pû me faire commettre cette erreur; c'est à Nessler même que j'eu suis en partie redevable. En effet, dans une notice qu'il a publiée relativement à ce dosage (*Zeitschr. f. anal. Chem.*, vii., 415, 1868), il dit en note; Vergl. z. B. Frankland und Armstrong, *Journ. Chem. Soc.*, (2), vi., 77, 1868.

Je n'ai pas remarqué les deux lettres z. B. (zum Beispiele) et de la mon erreur.

En recherchant le travail original de Wanklyn, à qui votre collaborateur attribue le procédé, j'ai trouvé, sauf nouvelle erreur, que ce n'est point lui, mais plutôt Chapman, qui en serait l'auteur, et qu'en réalité ce n'est ni l'un ni l'autre, mais bien W. A. Miller (*Journ Chem. Soc.*, (2), iii., 117, 1865; CHEM. NEWS, xi., 269, 1865; Le travail de Chapman (*The Laboratory*, i., 267, 1867) est postérieur de deux ans.

Ceux de Wanklyn, Chapman, et Smith, qui dâtent de la même époque (*Journ. Chem. Soc.*, (2), v., 445, 1867; *The Laboratory*, i., 241, 280, et 182, 1867; CHEM. NEWS, xvi., 7, 1867), si rapporteraient seulement, si j'en juge par les extraits que j'ai seuls à ma disposition (par ex. *Journ. f. prakt. Chem.*, cii., 333, 1867), aux applications du procédé à l'analyse des eaux, de même qui celui de Frankland et Armstrong (Voir aussi Bolley, *Journ. f. prakt. Chem.*, ciii., 498, 1868).

Ne désirant rien tant, comme je l'ai écrit dans la préface de mon "Traité," que de le compléter et le corriger lorsqu'il y a lien, je vous serais très reconnaisant de vouloir bien vérifier mes indications sur les publications originales que je n'ai malheureusement pas à ma disposition, et de me faire savoir si elles sont exactes, ou, dans le cas contraire, en quoi elles sont défectueuses.

Si vous croyez utile de publier quelque chose de ce qui précède, je vous autorise volontiers à le faire.

Veuillez agreer, Monsieur l'Editeur, l'expression de ma considération la plus distinguée.

DR. L. L. DE KONINCK.

Université de Liège,
le 13 Mars, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 10, March 5, 1894.

Preparation in the Electric Furnace of a Crystalline Calcium Carbide; Properties of this Novel Substance. — Henri Moissan. — This paper will be inserted in full.

Determination of the Density of Melted Magnesia. —Henri Moissan.—The specific gravity of this oxide increases rapidly with the temperature. It is:—At 350°, 3·1932; at dull redness, 3·2482; at white redness, 3·5699. In our experiments conducted in the electric furnace we have always observed that magnesia, purified by the Schlœsing process, could not be reduced by carbon. Hence we have constructed the interior of our furnaces with alternate plates of magnesia and carbon. On account of the easy reduction at the temperature of the arc of the alkaline earthy oxides and of uranium oxide by means of carbon, this stability of magnesia induced the author to re-determine its specific gravity when melted in the electric furnace. He obtained the following figures: — 1. MgO (blast furnace), 3·577. 2. MgO (furnace plates), 3·589. 3. MgO (fused mass), 3·654.

Experimental Study on the Expenditure of Energy Corresponding to the Chemical Action of Light.—Georges Lemoine.—Experiment shows us that for the exothermic and deeply-coloured mixture of ferric chloride and oxalic acid (both normal), the relation between the molecular work set in movement and the total absorption does not exceed a few ten-thousandths.

Atomic Weights of Precision Determined by means of Silver as Secondary Standard Substance. —G. Hinrichs.—If we compare the values of the atomic weights obtained with the absolute weight of the silver used, we see immediately that the variation of the atomic weight found is a very simple function of the weight of silver used.

Alloys of Iron and Nickel. — F. Osmond. — The author gives a tabular view of the composition of nine specimens of this alloy furnished by R. A. Hadfield. He ascertains their transformation points by the refrigeration method, their magnetic and their mechanical properties.

Action of Bromine upon Paraxylene.—J. Allain-Le Canu.—The author has successively obtained tolylene tribromide in orthorhombic laminæ melting at 116°, the aldehyd alcohol, an oily liquid, feebly aromatic, very soluble in ether, and a hydrazone, solid, of a light yellow, very unstable, and slightly soluble even in boiling water.

Cinchonifine.—E. Jungfleisch and E. Léger.—Cinchonifine ranks among the alkaloids insoluble in ether and also insoluble in alcohol at 50 per cent. It crystallises out of boiling alcohol in small anhydrous needles, brilliant and colourless. It is insoluble in water, ether, and dilute alcohol, very slightly soluble in the cold in alcohol and chloroform, but soluble in alcoholised chloroform. It melts at 273·6°. If strongly heated it is volatilised with decomposition. It is dextro-rotatory. Cinchonifine blues the tincture of litmus, but it does not redden phenolphthalein. The alkylic derivatives of cinchonifine crystallise distinctly. Dr. Hesse, after having contested the existence of cinchonifine, has recently described, under the name of homocinchonine, a base which presents great analogies with cinchonifine, and is obtained in a very similar manner.

Dibromogallanilide and its Triacetylic Ether.—P. Cazeneuve.—Dibromogallanilide is sparingly soluble in water, even at ebullition. The solution, on cooling, de-

posits crystals containing three molecules of crystalline water, which they lose at 100°. Dibromogallanilide is soluble in alcohol and in ether; it does not melt without decomposition.

Isomerism of Nitrobenzoic Acids.—Prof. Oechsner de Coninck.—In the group of the nitrobenzoic acids the ortho isomer approaches sometimes to the meta- and again to the para-isomer.

Zeitschrift fur Analytische Chemie.
Vol. xxxii., Part 5.

Preparation of the Pure Colouring-Matter of Litmus.—E. Mays.—From *Verhand. des Naturhist. Vereins Heidelberg* and *Journ. Chem. Soc.*

Preparation of Azolitmin Paper.—R. Dietral.—From the *Pharm. Zeitung* and *Journ. Soc. Chem. Industry.*

Occurrence of Starch in several Filter-Papers.—Th. Salzer (*Chemiker Zeituug*).—The papers under certain circumstances give with ferrous iodide a deep red colour. For the author's explanation of the non-appearance of blue starch iodide, the reader is referred to the original.

Separation of Cobalt and Nickel.—H. Herrenschmidt and E. Capelle.—See p. 112.

Solubility of Tartar in Alcohol.—W. H. Wenger.—A table taken from the *American Chemical Journal.*

Determination of Tannin.—Notices of a number of methods from the *Deutsch. Amer. Apotheker Zeitung*, the *Journal de Pharmacie*, the *Zeit. fur Hygiene*, the *Gerber*, the *Halle aux Cuiró*, from Brestewski's *Handwörterbuch der Pharmacie*, the *Journ. Soc. Chem. Industry*, the *Proceedings of the Franklin Institute*, and the *American Journal of Pharmacy.*

Determination of Proportion of Dirt in Market Milk.—Leopold Schulz (*Archiv. fur Hygiene*).—The author puts 1 litre milk from each dealer into a flask closed with a plug of wadding. On its arrival in the laboratory it is transferred to a measuring glass, covered with a piece of filter-paper and a glass plate, and allowed to stand for two hours. The milk is then carefully decanted off from the sediment down to about 30 c.c., the residue is made up to 1 litre with pure water, and again allowed to subside for one hour. It is then again drawn off, repeating this proceeding until all the dirt is left in pure water, which is then decanted off to about 100 or 150 c.c. The dirt is then collected in a tared filter, dried, and weighed. The dirt in the milk may be calculated as five times the dry residue. One litre of market milk was found to contain 3 m.grms. dirt at Würzburg, 3·8 at Leipzig, 9 at Munich, 10·3 at Berlin, and 14·92 at Halle. The richness of the milk in microphytes was surprising.

Determination of Moisture in Walls of Newly-Built Houses.—R. Emmerich (*Zeit. fur Hygiene*).—The plastered surface of the wall is measured, and circular discs of mortar of 0·5 square decimetre and of the entire thickness of the plaster are detached, weighed, and their moisture determined.

Carmine.—Sigmund Feitler (*Zeit. Angew. Chemie*).—Already inserted.

Determination of the Iodine Number.—Eugen Dieterich (*Helfenberger Annalen*).—The author considers the excess of 75 per cent of iodine required by Dieterich (*Chemiker Zeitung*) as unnecessary.

Reactions showing the Identity of Extracts.—E. Dieterich (*Helfenberger Annalen*).—A reference to the original.

Solubility of Balsams and Resins.—E. Dieterich (*Helfenberger Annalen*).—An extensive table of solubilities.

Examination of Commercial Oleic Acid.—E. Dieterich (*Helfenberger Annalen*).—The author finds that from 178·83 to 194·13 m.grms. potassium hydroxide are required to saturate the acid. Hence 90 per cent of oleic acid is the minimum in a good sample.

Determination of Chlorines in Urine.—Freund and Toepfer (*Centralblatt f. Klin. Medecin*).—Mohr's process is made available by adding to the urine 1-10th volume of a mixture of 3 per cent acetic acid and 10 per cent of sodium acetate.

Determination of Total Nitrogen in Urine.—A. Petit and L. Monfet.—The authors decompose 10 c.c. urine by Kjeldahl's method with 5 c.c. fuming sulphuric acid and a little mercury; add water when the mixture is cold and colourless, neutralise with soda, acidify with a few drops of sulphuric acid, make up to 50 c.c., and determine the nitrogen with hypobromite in 10 c.c. of the liquid.

Determination of Urea with Sodium Hypobromite.—E. R. Squibb (*Journ. Anal. Chem.*) and W. Colquhoun (Chemical News).

Determination of Uric Acid and Xanthin Substances in Urine.—W. Camerer.—The author's proposed method yields approximately the same values as Haycraft's process.

Detection of Sugar in Urine.—C. Kistermann (*Deutsch. Archiv. fur Klin. Medicin*).—For the application of the phenylhydrazin test, the author dilutes with five volumes of water.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 97.

Rational Use of Hops in Brewing.—E. Fleurent.—This paper is chiefly taken from a memoir to be found in the *Transactions* of the Institute of Brewing, London, and compiled by Messrs. Briant and Meacham. A table by Aimé Girard gives the proportions of hops per hectolitre of beer, ranging from 0·300 kilo. in the Louvain beer of Belgium to 0·800 in English pale ale and 1·000 kilo. in stout.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements after Easter:—Professor J. A. Fleming, Four Lectures on "Electric Illumination"; Professor J. W. Judd, Three Lectures on "Rubies—their Nature, Origin, and Metamorphoses"; The Rev. W. H. Dallinger, Three Lectures on "The Modern Microscope"; Mr. F. Seymour Haden, Two Lectures on "The Etching Revival"; Professor J. F. Bridge, Two Lectures on "Music" (1. Musical Gestures; 2. Mozart as a Teacher); Professor Dewar, Three Lectures on "The Solid and Liquid States of Matter"; Professor W. M. Flinders Petrie, Three Lectures on "Egyptian Decorative Art"; Mr. H. D. Traill, Two Lectures on "Literature and Journalism"; Mr. John A. Gray, Two Lectures on "Life among the Afghans"; Captain Abney, Three Lectures on "Colour Vision" (The Tyndall Lectures); Mr. Robert W. Lowe, Three Lectures on "The Stage and Society." The Friday Evening Meetings will be resumed on April 6th, when a Discourse will be given by Professor Victor Horsley on "Destructive Effects of Projectiles"; succeeding Discourses will probably be given by Professor J. J. Thomson, Dr. J G. Garson, Professor H. Marshall Ward, Dr. G. Sims Woodhead, The Rev. S. Baring-Gould, Professor A. M. Worthington, Sir Howard Grubb, Professor Oliver Lodge, Professor C. V. Boys, and other gentlemen.

Swiss Union of Analytical Chemists.—According to the *Chemiker Zeitung* the Swiss Union of Analytical Chemists will meet in the autumn at Zurich. The subjects discussed will include fats and soaps, the revision of the resolutions on butter, the examination of water (bacteriological and chemical), tea and coffee, and wine diseases.

Swiss Association of Naturalists.—It is announced that the Swiss Association of Naturalists—a body much resembling our British Association—will meet at Schaffhausen on July 29. 30, and 31. (It will be remembered that the German term "Naturforscher"—which we are compelled to render by "naturalist"—includes all persons who engage in research in any department of physical and natural science).

MEETINGS FOR THE WEEK.

TUESDAY, 27th.—Photographic, 8.
WEDNESDAY, 28th.—British Astronomical, 5.
THURSDAY, 29th.—Institute of Electrical Engineers, 8.

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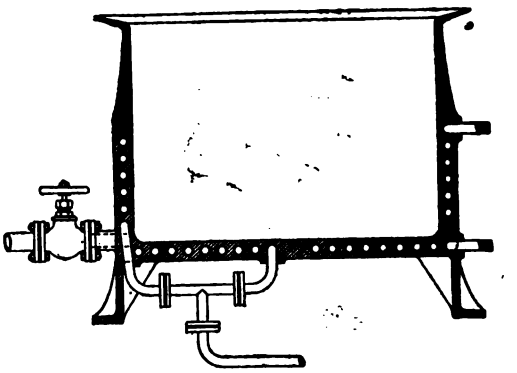

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co, Lim., London, 1894), says:—

P. 316. "An improved vessel for boiling oil, and suitable for many other kindred purposes, has been recently described by T. Frederking (CHEMICAL NEWS, London). A coil of stout piping is arranged in a casting mould, so that the molten metal forming the pan is cast round the coil, much as is done in the case of the water-tuyeres of a blast furnace. Steam at any pressure [or any other heating medium] being passed through the coil, the pan is heated up proportionately without any danger, the pressure bearing solely on the piping and not on the metal pan itself, whilst the well conducting metal walls allow the heat to pass readily. Temperatures up to 350° and 400° C. can be thus obtained."

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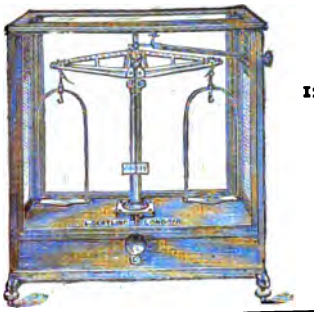

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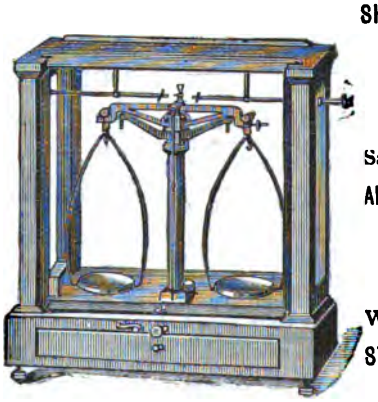

FIG. 3*a*.

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THE CHEMICAL NEWS.

VOL. LXIX., No. 1792.

THE ESTIMATION OF SMALL AMOUNTS OF BARIUM AND STRONTIUM IN SILICATE ANALYSIS.

By W. F. HILLEBRAND.

IN testing qualitatively for barium and strontium in the course of analysis of natural silicates it has probably been the custom to rely upon the spectroscopic examination of the ignited calcium oxalate, on the assumption that, notwithstanding the well-known greater solubility of barium and strontium oxalates over the corresponding calcium salt, the latter would carry down enough of the former to render detection of barium and strontium by aid of the spectroscope a matter of no difficulty.

This assumption in the case of strontium is well founded as I have observed times without number, but it may be entirely fallacious in the case of barium. The twice precipitated calcium oxalate of the analyses marked "later" in a succeeding paper (which will appear in our next issue) afforded a very strong spectroscopic reaction for strontium, but failed to give one for barium, although the oxide of this element was a constituent of the rocks up to 0·76 per cent, and simply because the latter had been entirely kept in solution by the large amounts of ammonium chloride present. This observation suggested at once an explanation for the apparent rarity of barium in the silicate rocks of the earth's crust, and opened up a field for investigation as to the best course to pursue in the separation and estimation of the three alkaline earth metals under the conditions generally prevailing in rock analysis; that is to say, great excess of calcium over barium and strontium in presence of magnesium and large amounts of sodium and ammonium chlorides.

Brief consideration sufficed to reject recourse to collective precipitation of the alkaline earths by ammonium carbonate because of the well-known incompleteness of such precipitation under the prescribed conditions.

It seemed better to seek a separation of barium at the outset. This conclusion was fortified by the results of experiments undertaken to ascertain the behaviour of strontium under conditions similar to and differing from the above. A large number of experiments were made with calcium, strontium, and barium separately, and then with mixtures of the former and either strontium or barium. The absolute amounts experimented with were kept low in order that the conditions usually obtaining in rock analysis might be as nearly as possible preserved. It was not for a moment expected that an exact method of separating considerable amounts of barium from either calcium or strontium would be discovered. The most that was hoped for was to work out a method suitable of application where relatively small amounts of strontium and barium occur with relatively large amounts of calcium. The outcome only in a measure fulfilled the hope raised by a few preliminary tests, but the results seem to be of sufficient interest to merit somewhat detailed description.

The precipitates were formed in ammoniacal solution at a boiling heat and were allowed to stand over night before filtering. They were washed but once or twice with cold water because of the very marked solubility of both strontium and barium oxalate in hot water, and even in cold water if the washing is prolonged. The filtrates were evaporated to dryness, ammoniacal salts were removed by heat, and after solution of the residue strontium and barium were precipitated as sulphates, the former after addition of alcohol. The sulphates were, when necessary, tested spectroscopically. The amounts of the different salts taken are purely arbitrary, except that the highest weights for BaO are the chemical equivalents of the highest for SrO.

From the Table (First Series) it is plain (1—3) that, as was to be expected, strontium is incompletely precipitated by ammonium oxalate in slight excess and that its solubility is markedly lessened by increase of the precipitant. Furthermore (4—6), that calcium if present in quantity exercises a notable effect in promoting completeness of precipitation. Finally, that with very small amounts of strontium and a great excess of calcium the precipitation of the former is practically perfect in presence of a sufficient excess of ammonium oxalate, irrespective of considerable variations in the ammonium chloride. Additional experiments in which 5—6 grms. of sodium chloride were added showed that this salt exercised a very slight but appreciable solvent effect on strontium oxalate. In entire absence of ammonium chloride, on the other hand, precipitation of as much as 0·004 grm. SrO is practically perfect in presence of 0·0560 CaO.

In the Second Series (11—17) the same action of precipitant and ammonium chloride that was observed in the first series makes itself manifest, only in much greater degree. Nos. 18—24 show in general the marked effect of small variations in the amount of precipitant, although an exception may be noted in 22 when compared with 21. Comparison of 19 and 22 with 11 and 15 respectively shows that the presence of calcium exerts no retentive effect whatever on the barium, in marked contrast with its behaviour towards strontium. With decreasing amounts of barium, the calcium remaining constant as well as the excess of precipitant, the slight influence of large variations in the ammonium chloride is apparent from Nos. 25—30. The general result is to show conclusively that considerable amounts of barium may be separated almost completely from calcium by a single precipitation with ammonium oxalate in presence of considerable ammonium chloride, provided the precipitant is used in slight excess only.* Additional tests have shown that sodium chloride, as with strontium, slightly facilitates the separation from calcium; also that a double precipitation will effect the quantitative separation of over 2 m.grms. BaO from 56 m.grms. CaO under the conditions of experiments 29 and 30. In cases like the last the whole of the BaO has been recovered from the filtrates and from the calcium as nitrate no trace of barium could be separated by ether-alcohol. It goes without saying that by increasing the ammonium chloride still larger amounts of barium may be equally well separated, as has been proven by numerous tests.

In endeavouring to apply the knowledge thus gained to the separation of barium from both calcium and strontium, which is the problem usually encountered in silicate rock analysis, difficulties at once suggest themselves, namely, those arising from the partial solubility of strontium oxalate in ammonium chloride, from the presence of 5 to 10 grms. of fixed alkali salts, whereby the exact recovery of barium and the strontium that may have gone into solution with it is rendered much less certain, and furthermore, from the increased solubility of the oxalates of the calcium group when, as is very often the case, magnesium is present in some quantity.

Of several experiments made to test the degree of accuracy attainable, first in absence of sodium chloride, then in presence of that salt and also of one of magnesium, thus reproducing the unfavourable conditions usually encountered in actual practice, the following will serve as fair examples.

1. CaO, 0·0560; BaO, 0·0023; SrO, 0·00095; $(NH_4)_2C_2O_4,H_2O$, one grm. in excess; NH_4Cl, ten grms.; total bulk of solution 250 c.c. Two precipitations under pre-

* This fact was first observed by the writer in 1884, and was mentioned in a footnote to p. 592, Appendix B, of Mr. S. F. Emmons's "Monograph on the Geology and Mining Industry of Leadville."

First Series.

	Amount taken calculated as oxide. SrO.	CaO.	$(NH_4)_2C_2O_4,H_2O$, amount in excess of that required for conversion of total bases to oxalates. Grms.	NH_4Cl. Grms.	Total bulk of solution. C.c.	SrO in filtrate. Weight,	Per cent.
1.	0·0343		½	10	250	0·0080	23·3
2.	0·0343		1	10	250	0·0045	13·1
3.	0·0343		2	10	250	0·0032	9·3
4.	0·0343	0·0560	1	10	250	0·0036	10·5
5.	0·0343	0·0560	1½	10	250	0·00275	8·0
6.	0·0343	0·0560	2½	10	250	0·0023	6·7
7.	0·00384	0·0560	1	5	250	0·0003	7·8
8.	0·00384	0·0560	1	10	250	0·0005	13·0
9.	0·0010	0·0560	1	5	250	Faint spectroscopic trace	
10.	0·0010	0·0560	1	10	250	,,	,, ,,

Second Series.

	Amount taken calculated as oxide. BaO.	CaO.	$(NH_4)_2C_2O_4,H_2O$, amount in excess of that required for conversion of total bases to oxalates. Grms.	NH_4Cl. Grms.	Total bulk of solution. C.c.	BaO in filtrate. Weight.	Per cent.
11.	0·0509		½	5	250	0·0230	45·2
12.	0·0509		1	5	250	0·0089	17·5
13.	0·0509		2	5	250	0·0070	13·7
14.	0·0509		4	5	250	0·0051	10·0
15.	0·0509		½	10	250	0·0457	89·8
16.	0·0509		1	10	250	0·0243	47·7
17.	0·0509		2	10	250	0·0138	27·1
18.	0·0509	0·0560	½	5	250	0·0436	85·6
19.	0·0509	0·0560	½	5	250	0·0293	57·5
20.	0·0509	0·0560	½	10	250	0·0489	96·0
21.	0·0509	0·0560	½	10	250	0·0458	90·0
22.	0·0509	0·0560	½	10	250	0·0463	90·9
23.	0·0509	0·0560	½	10	250	0·0346	68·0
24.	0·0509	0·0560	1	10	250	0·0206	40·5
25.	0·0135	0·0560	1	5	250	0·0109	80·7
26.	0·0135	0·0560	1	10	250	0·0106	78·5
27.	0·00906	0·0560	1	5	250	0·0074	81·7
28.	0·00906	0·0560	1	10	250	0·0079	87·2
29.	0·00226	0·0560	1	5	250	0·00177	78·3
30.	0·00226	0·0560	1	10	250	0·00197	87·2

cisely similar conditions. Found in filtrates, 0·00236 BaO, showing but the merest trace of strontium. Recovered from the lime, 0·00085 SrO holding fugitive spectroscopic traces of calcium and barium.

2. Precisely as in 1, with addition of 5½ grms. NaCl. In filtrates 0·0023 BaO, in lime 0·0006 SrO.

3. As in 2, with addition of 0·09 MgO. In filtrate 0·0023 BaO, in lime 0·0006 SrO.

It is apparent that the results are very satisfactory in 1, but that in 2 and 3 over 30 per cent of the SrO has escaped detection although all the BaO was recovered. The amounts of both BaO and SrO taken in these tests exceed what is met with in the great majority of igneous eruptive rocks, and the error in SrO may, therefore, in most cases be disregarded, for after all an absolute error of 25 or even 50 per cent in the estimation of a substance constituting only 0·1 per cent of a rock is ordinarily of small moment compared with the ability to certify to its presence with approximate correctness.

The procedure for the separation of the alkaline earth metals in silicate rocks as followed by myself with a fair degree of success for some time past, I will now outline, expressly premising, however, that it is not suitable for universal application, but that it seems to be the only one to meet the requirements of ordinary silicate analysis with anything approaching accuracy.

After a double precipitation, which should be made in any case, the ignited oxalate precipitate will contain nearly all the strontia and none of the baryta if the latter does not exceed 0·2—0·3 per cent of the rock. If a larger quantity than 0·3 per cent is present the precipitation by ammonium oxalate must be repeated or the rest of the barium subsequently separated from the strontium by ammonium chromate. The strontium is separated from the calcium by extracting the thoroughly dry nitrates (150—160° C.) by ether-alcohol, which, as clearly shown by the recent exhaustive researches of Fresenius,* is the only one of the older methods at all capable of yielding a fairly satisfactory result. Hereby, of course, any barium that might have been retained is also removed. The strontium weighed as sulphate should always be tested spectroscopically for barium, the barium sulphate likewise for strontium, either salt being brought into condition for making the test by reducing for a very few moments the whole or a part of the precipitate on a platinum wire in the luminous tip of the Bunsen burner, and then moistening with hydrochloric acid. If a trace of barium should be found with the strontium the error is

* *Zeitschr. Anal. Chem.*, xxix., xxx., xxxii., 1890, 1891, 1893. Separation by amyl alcohol as recommended by P. E. Browning, *Am. J. Sci.*, xliii., 50, and 314, 1892, has not been tried.

insignificant and may be balanced by the strontium remaining with the calcium nitrate.

Before destroying ammoniacal salts, either by ignition or by nitric acid, prior to estimation of magnesia, a few drops of sulphuric acid should be added to precipitate the barium* which otherwise might contaminate the magnesium pyrophosphate. I say *might*, for small amounts of barium, up to 3 or 4 m.grms. of oxide, will pass into the filtrate from the ammonia-magnesium phosphate. Only in exceptional cases have I ever found a trace of barium in the pyrophosphate after accidentally or purposely neglecting to effect a prior separation by sulphuric acid.

As to the barium itself it is improper to accept the amount thus separated from the magnesia as representing the total amount in the rock or mineral. It will almost always be found lower than the truth, probably for the reason that there are so many opportunities during the analysis for slight losses in the form of sulphate. Barium is best estimated in a separate portion which may also serve with advantage for the determination of titanium. The powder is decomposed in a capacious crucible with hydrofluoric and sulphuric acids, evaporation being repeated twice at least to ensure removal of all quartz. After volatilisation of the excess of sulphuric acid the dry residue is digested with water containing several cubic centimetres of sulphuric acid to surely retain all titanium in solution, and a few drops of hydrochloric acid, and the solution is allowed to settle for some hours. The ignited insoluble matter is evaporated with relatively much sulphuric and a little hydrofluoric acid till the latter is removed and a clear solution results, which is then poured into a few cubic centimetres of cold water. The precipitate will now be free from calcium in all probability, but may contain a little strontium, from traces of which it is easily freed by repeating once or twice the solution in strong acid and re-precipitation by water.† Unchanged weight after the final precipitation is evidence of purity of the barium sulphate, and the spectroscope should confirm this. These last mentioned manipulations require little expenditure of time even when they have to be repeated, and the result is usually eminently satisfactory. If the first weight of the barium sulphate is but one or two m.grms. it is rarely necessary to purify the salt further.

Such is the procedure when only small amounts of barium and strontium have to be estimated. Should they be present in amount exceeding, say, two m.grms. for SrO, and four m.grms. for BaO, or should with smaller contents a high degree of accuracy be desired, the already difficult analysis presents still greater difficulties. In such cases there remains no other way than to combine the barium and strontium found in the filtrates from the calcium oxalate with the strontium and barium separated from the oxalate itself, and to apply to the mixture the ammonium chromate method of separation as prescribed by Fresenius (*l. c.*). The practiced eye readily learns to judge by spectroscopic test of the ignited and weighed calcium oxide whether strontium is in sufficient quantity to necessitate this course, and the separate determination of barium as above described will decide with regard to that metal.—*Journal of the American Chemical Society*, xvi., No. 2.

British Sherry.—According to the *Medical Press* the Glamorganshire Public Analyst reports on a so-called "British sherry" which fell into his hands, that it was composed of sugar, a little essence (?), and calcium bisulphite. As it contained no alcohol it may perhaps receive the sanction of the temperance interest.

* The barium sulphate thus formed is not separated by filtration till after destruction of the ammoniacal salts, and, if this has been effected by nitric acid, not until after evaporation to dryness.

† If the rock happens to contain zircon this may, and probably will, remain with the barium sulphate until removed by appropriate means.

UPON THE SEPARATION OF THORIUM FROM THE RARE EARTHS OF THE CERIUM AND YTTRIUM GROUPS BY MEANS OF POTASSIUM HYDRONITRIDE.

By L. M. DENNIS and F. L. KORTRIGHT.

WHILE engaged in other investigations on the rare earths, it was observed that when a solution of potassium hydronitride, KN_3, was added to the neutral nitrate solution of the earths extracted from the mineral sipylite, a white flocculent precipitate resulted, while by far the larger portion of the bases remained in solution. Both the original solution and the filtrate from the potassium-hydronitride precipitate showed strong erbium absorption-bands before the spectroscope. The precipitate was washed with water and dissolved in dilute nitric acid; this solution showed no absorption-bands.

From this it was evident that the potassium hydronitride had effected a fairly sharp separation of certain oxides from the mixture of earths present in the original solution. To ascertain the nature of the precipitate, the experiments were repeated with larger amounts of material, the earths from monazite being used, as our supply of sipylite was quite small.

Monazite sand from Brazil* was freed as far as possible from intermixed menaccanite by washing in a gold-washer's pan, and was then heated for several hours with concentrated sulphuric acid. The residue was introduced, in small amounts at a time, into ice-water, and was allowed to stand for several hours with occasional stirring. The clear supernatant liquid was then drawn off, and the ice-cold solution was precipitated at once with oxalic acid. The oxalates of the rare earths thus obtained were washed by decantation with hot water containing about 1 per cent of hydrochloric acid, until the wash-water gave only a faint reaction for iron when shaken with potassium sulphocyanate and ether. The oxalates were then dissolved in concentrated nitric acid, most of the acid in excess was evaporated off, and the residue was dissolved in water, diluted, and precipitated by ammonium hydroxide. This precipitate was washed until free from lime and was then dissolved in hydrochloric acid. Hydrogen sulphide was passed through the hot solution for four hours. The flame was then removed, the current of hydrogen sulphide being continued over night. The very slight precipitate which formed was removed by filtration, the filtrate freed from hydrogen sulphide by heat, and the earths again precipitated by oxalic acid. This precipitate was washed with hot water containing a little hydrochloric acid to free it from the traces of iron which it still contained, and was then dried and ignited. The oxides thus purified were dissolved in nitric acid, most of the acid in excess was removed by evaporation, and the solution after dilution with water was nearly neutralised with dilute ammonium hydroxide. To this solution potassium hydronitride was added until a precipitate ceased to form. The white gelatinous precipitate settles quite readily if the solution of the earths be largely diluted before the hydronitride is added, or if a rapid current of air is driven through the solution after the addition of the reagent. The precipitate was washed by decantation with water until free from the mother-liquor and potassium salts. It was then dissolved in hydrochloric acid, and the solution precipitated by oxalic acid.

A portion of this precipitate, dissolved in nitric acid and evaporated to dryness, yielded a residue which gave no lines when tested in the Bunsen flame before the spectroscope. Moreover, the concentrated neutral nitrate solution of the precipitate showed no absorption-bands. A portion of this solution, diluted with an equal volume

* For the large amount (some 70 pounds) of this mineral placed at our disposal, we are indebted to the generosity of Professor Ricketts, of Columbia College, and Mr. G. O. Gordon, of New York City.

of water and boiled with lead dioxide, remained colourless, showing the absence of any appreciable amount of cerium.

From these experiments it seemed probable that the earth precipitated by potassium hydronitride was thoria. To test this supposition, the rare earths extracted from a sample of Norwegian thorite were dissolved in nitric acid, potassium hydroxide was added in excess, and chlorine was passed through the liquid and suspended precipitate for 24 hours. The precipitate still remaining was then filtered off, washed thoroughly, dissolved in hydrochloric acid, the solution precipitated by pure oxalic acid and the precipitate again carefully washed. To the nearly neutral nitrate solution prepared from this oxalate, potassium hydronitride was added in excess, A voluminous gelatinous white precipitate resulted. On adding ammonium hydroxide to the filtrate from this precipitate only a very slight precipitate appeared after some hours.

The equivalent of the earth precipitated by the potassium hydronitride from the monazite earths was then approximately determined by converting the earth into the oxalate, drying this at 100° C., weighing, igniting to constant weight, and weighing the resulting oxide. Considering the composition of the oxalate dried at 100° C. to be $Th(C_2O_4)_2.2H_2O$, three determinations gave Th=232·1, 232·7, 232·4 (O=16), the results agreeing fairly well with the figures adopted by Ostwald as the most probable, namely, Th=232·4.

Early in the work it was found that the potassium-hydronitride precipitate, on being heated on a platinum crucible-cover in the flame, simply dried down to a white powder without showing in the least the explosive quality possessed by other hydronitrides described by Curtius. A neutral solution of thorium nitrate was then prepared by adding to the slightly acid thorium solution ammonium hydroxide until a faint permanent precipitate formed. The precipitate was filtered off, and to the filtrate was added a neutral, odourless solution of potassium hydronitride. The usual precipitate resulted, and the characteristic odour of hydronitric acid became at once discernible, showing that when the thorium is precipitated by potassium hydronitride, some at least of the hydronitric acid is set free. A portion of the precipitate dissolved in nitric acid,* neutralised with potassium carbonate and acidified with acetic acid, gave no precipitate with silver nitrate. A test made in the same way with some potassium hydronitride gave a heavy precipitate. It thus appearing that the precipitate might be thorium hydroxide, an analysis was made of a freshly prepared portion. The precipitate was washed with water to remove the potassium salt, and was then filtered in an atmosphere free from carbon dioxide. The precipitate was dried in a tube at 100° in a current of air free from carbon dioxide. Weighed portions of the precipitate were then ignited and the residual thorium oxide weighed.

	Calculated for $Th(OH)_4$.	Found. I.	II.	III.
ThO_2 ..	88·01	84·95	85·52	85·72

Although these results agree better with the hydroxide than with any other compound of thorium to be expected here, their great variation from the theoretical percentage made it seem probable that in spite of the precautions taken, the precipitate had absorbed carbon dioxide during the analysis. This supposition was borne out by the fact that on treating the dried precipitate with nitric acid, a gas was evolved which caused a turbidity in baryta-water. A repetition of the analysis was unfortunately impossible, as our supply of potassium hydronitride had been exhausted. A large amount of the reagent is now being made, with which further investigation of the nature of the precipitate and of the completeness of the separation from the other earths will be carried out.

* No odour of hydronitric acid was perceptible when this was done.

Preparation of the Potassium Hydronitride.

The hydronitric acid was prepared by the method of Wilhelm Wislicenus (*Ber. d. Chem. Ges.*, xxv., 2084), the form of apparatus used being a slight modification of that proposed by Hopkins (*Science*, xxii., No. 544, p. 1). A sheet-iron cylinder, 12 c.m. high and 8 c.m. in diameter and closed at the bottom, is set into a large cylinder 15 c.m. high and 13 c.m. in diameter, the latter acting as an air-bath. The inner cylinder projects a short distance above the top of the large cylinder, and is provided with a tightly fitting iron cover. In this cover are three openings, one for the introduction of the ammonia or nitrous oxide, another for their escape, and the third for the thermometer. About 25 grms. of metallic sodium is put in a small iron dish, and this is then placed in the inner cylinder. Dry ammonia gas is passed in, and the bath is heated by a Bunsen burner placed under the outer cylinder, to a temperature somewhat above 300° C. When the molten sodium has been transformed to the amide, the temperature is lowered to from 200° to 230°, and nitrous oxide is run in. The sodium hydronitride is then dissolved in water, the solution acidified with dilute sulphuric acid, and the hydronitric acid is distilled over into water. The aqueous solution of the acid was then added to a solution of potassium carbonate until the reaction was quite strongly acid, and this was used in making the precipitation.—*American Chemical Journal*, xvi., No. 2.

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

SECOND PAPER: THE ANALYSIS OF BARIC CHLORIDE.

BY THEODORE WILLIAM RICHARDS.

(Continued from p. 137.)

Ratio of Metallic Silver to Baric Chloride.

IN determining this ratio the solubility of argentic chloride plays a much more damaging part than in the determination of the previous one. The uncertainty may easily become as great as thirty or forty m.grms. in the weight of the silver—an amount so enormous as to render accurate determination apparently impossible. Aside from this uncertainty, due to the existence of the two end-points, the observation of the point at which a drop of one solution or the other absolutely ceases to produce a precipitate is a very trying matter. The physical condition of the observer, and his practice in observation of this sort, have much to do with his determination of the presence or absence of a faint cloud at the top of the vessel under observation. The phenomenon is one which gradually fades away as more and more silver or hydrochloric acid is added, the last opalescence appearing only after some time. Often when no cloud is visible at the end of an hour, a very evident one is to be seen in two hours. The amount of light at hand is also an important factor in the determination. Temperature produces a very important effect on the solubility of argentic chloride, and this effect is tripled when it is referred to the solution which is being added. The results are thus far less satisfactory than similar results obtained with the bromide.

For preliminary experiments the method used by Stas in his early analyses ("Untersuchungen," &c., Leipzig, 1867) was adopted. The method consisted in the addition of an excess of silver to the solution of baric chloride, a standard solution of hydrochloric acid being used to determine this excess. At first the atomic weight thus obtained corresponded very closely to that obtained by

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*,

the last ratio, but as the work proceeded the apparent atomic weight of barium steadily rose. The reason for this anomaly was not clear for a long time; but in the end it was evident that the apparent accuracy of the first results had been due to the mutual elimination of two opposite errors. The occlusion of argentic nitrate by argentic chloride tended to require too much silver, and the method of titration required almost equally too much hydrochloric acid. When more care was taken with regard to the dilution of the argentic nitrate, and as the observer became more and more practised in the delicate observation of the end point, the first error steadily decreased and the second steadily increased. Hence, they no longer counterbalanced one another. A long time was spent in finding that this first method, used by Stas in his early analyses of lithium, sodium, potassium, and ammonium chlorides, was quite false. Even relative results by this method, such as Stas's comparison of the different varieties of silver, can have no important value, because it is well-nigh impossible to make all the conditions absolutely constant. It is almost needless to say that these remarks apply only to this early method, and not to Stas's later work. Naturally he made errors at first. It is much to be regretted, however, that he did not point out more clearly afterwards the serious nature of these errors, which he clearly appreciated. Most of the investigations of Stas remain models of precision, and no one who has not attempted practically to follow in his footsteps can form an adequate idea of the greatness of his success.

Stas's study of the "Statics of Argentic Chloride" has been already referred to. As a result of this long and valuable series of experiments, he concluded that the true end-point must be half way between the two end-points obtained by titrating in opposite directions. When this true end-point had been reached, he found that the supernatant liquid was rendered equally opalescent by equivalent amounts of hydrochloric acid and argentic nitrate. These conclusions suggested two possible methods for the solution of the problem before us; and it is worthy of remark that at least one of these methods had been suggested by Mulder fifteen years before Stas's publication ("Silberprobirmethode," p. 94).

The unsatisfactory results obtained by the old method inclined one to subject the newer methods also to a careful testing before going further; accordingly a long series of experiments, not unlike those described by Stas, were instituted to prove them. In the first place, pure thoroughly-washed argentic chloride, which had been made and kept in darkness, was shaken with a dilute solution of pure baric nitrate and nitric acid; and then the two end-points were determined by adding first hydrochloric acid and afterward argentic nitrate until no more cloudiness could be observed in either case. The results were not very satisfactory, for a reason which appeared later. Nevertheless, many experiments were made in this way, showing that the observation of Stas was at least approximately true. The observation with regard to the equality of opalescence could not be confirmed at once, because the method requires much practice; but in the end the confirmation of it was much more satisfactory than the previous one. It was clear, however, that both methods depended upon a question of judgment rather than upon definite weighing or measuring.

In default of a more satisfactory method a series of experiments upon the atomic weight of barium was made by determining both end-points and taking the mean as the true one, according to Stas's second method. During this series a curious fact became manifest. As the alternate addition of hydrochloric acid and silver nitrate proceeded, the necessary amount of each solution increased to an enormous degree. For instance, in Experiment 33 the first difference between the end-points was 16 m.grms. of silver, while the third was as much as 34 m.grms. This change was probably due to the fact that the argentic chloride produced by the successive additions of the solutions was of the more soluble flaky variety, while the greater part of the precipitate had been so thoroughly shaken before as to become much less soluble. A larger amount of the salt in solution naturally required more of each reagent to precipitate it. This phenomenon was the chief cause of uncertainty in the attempt to confirm Stas's results. Probably the reason for his overlooking it lay in the fact that he rarely titrated backward and forward many times with the same solution.

(To be continued).

THE QUESTION OF THE OCCURRENCE OF HYDROGEN PEROXIDE IN ATMOSPHERIC AIR AND IN ATMOSPHERIC WATERS.*

By EM. SCHÖNE.

(Continued from p. 138.)

As for the second not less characteristic and even more sensitive reagent absolutely proving the existence of atmospheric hydrogen peroxide, *i.e.*, the combination of guiacum and diastase (commonly called extract of malt), Iloswa entertains a thoroughly erroneous conception. He says (p. 380): "I have observed that on mixing with the solution of hydrogen peroxide a little tincture of guiacum and then some extract of malt, the white colour is certainly transformed into blue, but that this transformation takes place equally with pure water on agitating the solution with air, and better still on operating with a dilute solution of potasium nitrite."

This declaration proves that Iloswa has left out of consideration a few circumstances which he would not have overlooked if he had made himself more closely acquainted with the literature of this reaction—certainly very copious—and especially with that of guiacum resin.

That on the addition of extract of malt he obtained a blue colour with the resin distributed in pure water might be:—

1. Because his tincture was not rightly prepared, the resin either not being taken from the middle of a larger piece, or the alcohol used having been exposed to light.
2. Or because the tincture used had not been recently prepared.
3. Or because the reaction was undertaken in an atmosphere containing traces of ammonia.
4. Or because the mixture was exposed to the influence of sunshine.
5. Or because the extract of malt was contaminated with some one of the many substances which occasion a colouration of the resin.

In any case it is certainly established, both by earlier researches and by investigations which I have recently conducted with the utmost care, that an emulsion obtained with correctly and recently prepared tincture of guiacum and pure water is, on the addition of a correctly prepared solution of diastase, not coloured in the slightest in diffused daylight in the course of many hours, and in the dark not in the lapse of several days.

If Iloswa obtained a more intense colouration of the resin on adding a dilute solution of potassium nitrite, this might be occasioned by the presence in the solution of free alkali—which is not seldom the case in commercial potassium nitrite—of which a very small trace suffices to colour the guiacum resin a greenish blue, when it is quite indifferent whether diastase is present or not.

Neutral ammonium nitrite (obtained by mixing equivalent proportions of silver nitrite and ammonium chloride) behaves quite indifferently with guiacum, even on the addition of diastase.

* *Berichte der Deutschen Chemischen Gesellschaft*, xxvi., p. 3011.

Free nitrous acid, as also ozone, chlorine, and the like, colour guiacum tincture alone without the addition of diastase, and are thus sharply diagnosed from hydrogen peroxide, which does not colour the resin if *alone*, but occasions the colour on the addition of diastase, blood corpuscles, or some other "exciter."

As regards the sensitiveness of this reagent, I had previously found that with it we may demonstrate one 20-millionth part (0·05 m.grm. hydrogen peroxide in a litre). But if for the watery extract of malt we substitute a mixture of 25 parts of water with 1 part of the solution of diastase in glycerin (as proposed by A. Stutzer and used by C. Faubenbach for rendering starch soluble), we may demonstrate with certainty 0·03 m.grm. hydrogen peroxide in a litre, or three hundred millionths. An observer well acquainted with the reaction on comparison with a check specimen can distinguish even two hundred millionths.

These two reagents, therefore, contrary to the contentions of Iloswa, are absolutely characteristic for hydrogen peroxide, and sufficiently sensitive, on proper management, to show its presence both in the natural atmospheric downfall, as also in artificial dew (or hoar frost), which was prepared for the demonstration of the vapour of hydrogen peroxide in the air.

I have taken the trouble—which to those familiar with the reactions of hydrogen peroxide may seem needless—to submit the trustworthiness of the two above-mentioned reagents to a new all-sided experimental investigation—especially as regards their behaviour with free and combined nitrous acid. On the results of this enquiry a full report will shortly appear in one of the journals devoted to analytical chemistry. I shall there describe more in detail the procedure to be observed in applying these reagents to the demonstration of hydrogen peroxide in atmospheric waters.

(To be continued.)

ON THE ORIGIN OF MOSS GOLD.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

In 1876 I had the privilege to read a paper before this Society "On the Formation of Moss Gold and Silver" (*Journ. Roy. Soc. N. S. Wales*, 1876, vol. x., p. 125); since that time the matter has had to be more or less laid aside; but as opportunity offered, the investigation as to the cause of the moss-like form of gold met with during the roasting of auriferous mispickel has been proceeded with, and in this note the results are given of additional experiments which appear to afford a solution as to the peculiar forms assumed by the gold, described in the above-mentioned paper.

Without going into details, it may be mentioned that the paper referred to contained the results of experiments made with the object of ascertaining the condition in which the gold existed in certain rich specimens of mispickel, obtained from a mine near Orange in New South Wales; these specimens were roasted in a muffle so as to drive off the arsenic and sulphur, and with the intention of afterwards dissolving away the iron oxide with hydrochloric acid so as to ascertain whether the gold was crystallised; on removing the specimens from the muffle, exudations of ochre-coloured matter were seen on their surfaces. These exudations on closer examination were found to be gold in cauliflower-like aggregations, and under the microscope these were seen to be made up of spicules and spirals of gold (afterwards proved to contain some arsenic); the temperature of the muffle was kept between the fusing-points of tin and zinc, so as to make quite certain that it was never hot enough to fuse gold. The residual iron oxide never showed any traces of fusion.

For these and other reasons I concluded, in my former paper, that the gold had not been fused; my later experiments, however, show that although the temperature was insufficient to fuse gold, it was quite high enough to melt the very fusible compound of gold and arsenic which was either present in the specimens under examination or formed during the roasting.

In the *Mineralogical Magazine* for 1877 and following years, there are several communications from Mr. T. A. R. Readwin upon the formation of moss gold. He is of opinion that metallic growths of gold, silver, electrum, and native copper take place at ordinary temperatures, and cites a number of cases of specimens in his cabinets which appear to have "grown" since they have been in his possession. In the case of easily oxidisable sulphides rich in gold, this is probably not impossible.

In the former paper an experiment is given in which gold was fused in a crucible with mispickel under borax; on roasting the auriferous button, moss gold was obtained as from the natural specimens, but of much smaller dimensions. The following additional experiments have been made which more conclusively prove that mispickel, iron pyrites, and other sulphides take up gold when fused with it, and in the case of the mispickel give up the gold, on roasting, in moss-like forms.

The following experiments with gold and various sulphides were made in 1877; in each case the sulphide was loosely mixed with the gold (sovereign gold rolled into a thin ribbon and cut up into minute squares), or the gold was only laid on the top and the whole covered with a layer of borax and fused.

Description and weight of sulphide, in grms.	Weight of gold used, in grms.	Percentage of gold used.	Weight of gold separated as a button, grms.	Percentage of gold in regulus.
30 Mispickel ..	3·25	10·80 (*c*)	none	3·60 (*a*)
30 „ ..	1·20	4·00	1·05	not assayed
30 „ ..	0·90	3·00	0·75 (*e*)	not assayed
25 „ ..	0·50	2·00	0·3	0·80 (*a*)
30 „ ..	0·30	1·00	0·15 (*f*)	not assayed
30 Iron pyrites ..	3·25	10·80	none	12·25
25 „ ..	0·50	2·00	0·39	0·44 (*b*)
80 „ ..	1·17	1·46	none	0·80 (*d*)
80 Copper pyrites	1·17	1·46	none	1·00
80 Antimonite ..	1·17	1·46	none	4·42
80 Galena	1·17	1·46	none	1·20

(*a*) The regulus of mispickel in each case showed a crystalline structure on fracture, and the fracture, under the microscope was seen to be studded with gold; there was also some moss gold over the surface of the button and in the cavities. On roasting, the mispickel regulus always yielded moss gold.
(*b*) A white brittle button separated during fusion, containing streaks of gold—weight, 0·3 grm.
(*c*) Precipitated spongy gold was used in this case.
(*d*) Yellow malleable button.
(*e*) Very brittle, intersected with a white crystalline vein.
(*f*) Colour nearly white.

In some cases the percentage of gold found in the product or regulus was greater than that added; this, of course, was due to a part of the original mineral having been removed in the slag or volatilised. Moss gold was only obtained from the regulus of mispickel; none of the other sulphides yielded any.

The above experiments, however, only show that an artificial mixture of gold and mispickel will yield moss gold.

* A Paper read before the Royal Society of New South Wales.

The next series of e xperiments was upon the preparation of sulpharsenide and arsenide of gold and the production of moss gold from them.

Gold, Arsenic, and Sulphur.

Experiment 1.—A solution was made of sodium chloraurate and sodium arsenite, and hydrogen sulphide passed; the precipitate of the mixed sulphides of arsenic and gold and free sulphur was dried and roasted, a cauliflower-like residue of gold was left similar to that exuded by auriferous mispickel, which under the microscope was seen to contain a few fine filaments.

Experiment 2.—The experiment was repeated with the same result.

Experiment 3.—Some of the mixed sulphide of gold and arsenic was compressed into small cylinders, by means of a steel diamond mortar, and two of these were carefully roasted at the mouth of the muffle. In both cases the gold was left as a porous mass with sponge-like perforations running through it in all directions—with filaments of gold visible under the microscope.

Gold and Sulphur.

Experiment 4.—Some experiments were made in 1878 upon gold sulphide obtained by passing hydrogen sulphide through the solution of the sodium chloraurate; this sulphide on roasting yielded ordinary dull brown gold, but in parts it appeared to be more or less crystallised. This experiment was repeated more than once with the like results.

Experiments with Gold and Arsenic.

In making the arsenide of gold, in the first experiments in glass tubes, the gold foil was placed in a porcelain boat and the vapour of arsenic driven over it, but it was afterwards found that the boat could be dispensed with. A piece of hard glass three-quarter inch combustion tubing was closed at one end and some metallic arsenic filled in to about one inch, then a plug of asbestos, and upon this the spirals of gold-foil were placed; the tube was held in an inclined position in a retort stand, and the arsenic volatilised by a Bunsen flame; when the air had been displaced by the arsenic vapour, the gold was heated to redness by the blowpipe; it quickly began to fuse and to run down upon the asbestos. (The blowpipe flame was quite incapable of fusing the gold by itself in the tube, even when the blast was kept up for an hour or so and the tube softened out of shape, but in the arsenic vapour the gold ran down with great readiness at a dull red heat). The compound of gold and arsenic formed is very fusible and remains liquid for some little time after removal from the flame and when it has much cooled down; the globules are large and much rounded, so that its surface tension is great, like that of the liquid alloy of potassium and sodium; in fact the appearance of the fluid arsenide reminded me very much of that alloy, except that the arsenide is of a yellow colour.

The gold arsenide solidifies suddenly on cooling (superfusion) and sometimes spirts a good deal, the small projected globules attach themselves to the glass tube, but can be readily removed. The cooled mass is often coarsely crystallised on the surface, when it presents a bright lustrous gold colour and appearance, but underneath it is seen to be honeycombed in every direction. In the cavities the microscope shows spirals and spiculæ of gold or of the gold-like arsenide. It is very brittle and breaks readily; inside it is crystalline and may be cavernous, in places there are patches of a bright metallic grey colour. This may be due to the presence of free arsenic or to a grey alloy, but I have not yet had time to determine this. In other cases the resulting compound has the dull ochre colour of moss of precipitated gold.

The alloy first formed by simple fusion seems to greedily absorb more arsenic, *i.e.*, when a piece of arsenic is pushed up against it; the alloy wets the arsenic and on slowly withdrawing the arsenic the alloy follows it like a streak of water, for from one-quarter to half an inch. The apparent absorption of the arsenic may be partly due to the arsenic being volatilised by contact with the fluid alloy. (See Experiment No. 9).

Experiment 5.—In the next experiments for the formation of the gold arsenide, arsenic was filled into a hard glass three-quarter inch tube to the depth of one to one and a half inch, and a plug of glass-wool placed upon it; the gold plate or foil was next dropped in, followed by another plug of glass wool; the tube was then rendered vacuous, sealed, and heated to redness in a combustion furnace. On cooling, the spirals of gold were seen to have fused down into one large globule, one-third inch across; scattered about were a number of small globules which were flattened and attached to the glass tubing, extending over two inches of the length of the tube; this scattering seems to have taken place on the solidification of the large globule, and was probably due to the expulsion of an excess of arsenic. This experiment was repeated with a similar result; in the next experiment mispickel was used as the source of arsenic. On cupellation the first globule yielded 90·36 per cent of gold and 9·64 of arsenic (by difference). The globule of gold arsenide from the mispickel yielded only 1·82 per cent of arsenic.

It was afterwards found that the combination could be brought about by heating the arsenic and gold, separated by an asbestos plug, in an ordinary small hard glass tube of one-quarter inch bore; in the first trial the alloy melted down into a pear-shaped globule, which was very brittle and crystalline. On cupellation, the loss was equal to 5·54 per cent of arsenic.

Experiment 6.—Next 0·411 g. of pure gold was treated as in the last experiment; on removal from the lamp after I thought it had solidified, the globule still remained fluid, for an air bubble was seen to slowly make its way through the globule (as in a tube containing mercury); the globule solidified immediately, but the channel caused by the bubble was left. In this channel, minute spicules and spiral filaments of gold (moss gold) were seen when examined under the microscope.

The globule was weighed and found to have taken up 6·16 per cent of arsenic; the amount was really larger, but some of the alloy was lost by spirting on solidification. On cupellation of part of this globule the loss was equal to 7·5 per cent of arsenic.

Afterwards larger amounts of gold were converted into arsenide in this way. On introducing cold gold into the arsenic vapour it became coated with a grey deposit of metallic arsenic, but as it became hotter the gold recovered its usual colour and lustre, but as soon as the gold became just red-hot it rapidly fused down at the edges, just as when a strip of lead is held in a flame. In dealing with this larger quantity of gold in the large combustion tubing (three-quarter inch diameter) it was found necessary to use a gas blowpipe, as a Bunsen was not quite sufficient.

Experiment 7.—In this case the globule from 1·3627 g. of gold was shaken just as it was about to solidify, the whole suddenly became solid, with strongly marked crystalline surface, and of a very bright lustrous gold colour, but cavernous at the base and exceedingly brittle. On cupellation, it lost weight equal to 4·61 per cent arsenic.

Experiment 8.—On roasting and fusing a portion of the alloy obtained in this experiment in a muffle without cupellation, it lost weight = 3·29 per cent of arsenic, although it showed, when fractured, grey specks of either arsenic or a grey alloy.

Experiment 9.—In this case after a globule of the arsenide had been formed, fresh supplies of arsenic were pushed down against the molten alloy (the supply of arsenic vapour from the bottom of the tube being still kept up), when it was apparently rapidly absorbed by the fluid alloy, the alloy "wetted" the plate of arsenic at once, and when the plate was drawn slowly backwards followed it as a streak (like water) to about one-third inch in distance.

As the quantity of arsenic increased the alloy became

less fluid and less brilliant in lustre; whether much more arsenic was really absorbed and whether the arsenic was only volatilised by contact with the fluid alloy is difficult to tell. On solidifying, the alloy seems to expel arsenic vapour, and this condenses on the inside of the tube, but it is difficult to watch the operation because the atmosphere of arsenic vapour used for producing the alloy also condenses on the sides of the tube soon after its removal from the lamp.

This specimen on cooling was of a dull brown colour, just like the moss gold from mispickel, very hollow and blown out into a secondary globule on one side; the cavities contained spicules and spirals of moss gold.

It was very brittle, and on cutting it with a sharp chisel more or less powder was produced; the fracture was coarsely crystalline and of a dull gold colour, which under the microscope was seen to be intermingled with grey. On cupellation it lost weight = 3·2 per cent of arsenic.

Experiment 10.—In this case a weight of 7·3674 g. of fine gold was alloyed with arsenic; on the gold first fusing down or "burning" in the arsenic vapour a very fusible alloy was formed, but this, like the last, became less fusible as more arsenic (solid) was pushed into it (the arsenic had been previously sublimed in glass tubes for this purpose), and on cooling it lost its metallic lustre, became covered with cauliflower-like growths, and spirted a good deal. The cavities contained the usual spicules and spirals of moss gold. On cupellation the loss was equal to only 2·8 per cent of arsenic.

Experiment 11.—This arsenide was of the colour and lustre of freshly cast bronze. Loss = 5·9 per cent As on cupellation.

Experiment 12.—Also of a bronze colour. Loss = 4·9 per cent of As.

Experiment 13.—Of a bright gold colour and matt lustre; this had formed directly in contact with the arsenic and had solidified on the arsenic itself—the alloy was pitted in places and had a very strong resemblance to a nugget. Its fracture showed a few grey streaks mixed with the gold. On cupellation it lost weight = 9·9 per cent arsenic.

Experiment 14.—The moss gold obtained by roasting the auriferous mispickel from the New Reform Mine, Lucknow, was cupelled with lead, when 2·3668 grms. lost 0·057 or 1·98 per cent.

From the foregoing experiments it will be seen that the amount of arsenic taken up by the gold varies very much; thus the alloy from Experiment 5 (from arsenic and gold) lost 9·64 per cent arsenic, and from mispickel and gold 1·82 per cent of arsenic.

				Per cent.	
Experiment	6	(from arsenic and gold)	lost	7·5	of arsenic
,,	7	,, ,,	,,	5·61	,,
,,	8	,, ,,	,,	3·29	,,
,,	9	,, ,,	,,	3·2	,,
,,	10	,, ,,	,,	2·8	,,
,,	11	,, ,,	,,	5·9	,,
,,	12	,, ,,	,,	4·9	,,
,,	13	,, ,,	,,	9·9	,,
,,	14	,, ,,	,,	1·98	,,

The lowest containing only about 2 per cent, and the highest nearly 10 per cent of arsenic.

While the arsenic is hot it feels sticky when touched with an iron wire, and the fragments cohere to a certain extent.

The excess of arsenic left in the lower part of the tube, as well as the sublimed arsenic, shows well developed crystals.

Experiment 15.—Precipitated gold was mixed with powdered purified arsenic in about equal bulks, and compressed into small cylinders by means of a diamond mortar, and then roasted slowly in a muffle; the gold was left as a porous cylinder, but with excrescences of moss gold in places and lining the cavities.

Experiment 16.—Moss gold was also obtained by roasting a cylinder composed of mispickel 1 g. and 0·75 g. of precipitated gold.

Experiment 17.—Gold 0·75 g., arsenic 0·5 g., and sulphur 0·5 g., were compressed; on roasting it at once fused down into an irregular cake with a very cavernous and spongy structure; the surface was like that of moss gold, and under the microscope the usual spicules and spirals were seen. The cupel used as a support was stained of a purple tint, and this penetrated to nearly one-eighth of an inch deep, just as if the gold had been in solution.

Experiment 18.—To ascertain if finely-divided gold would burn in arsenic vapour, I introduced some gold leaf; it combined in much the same way as the foil, but more quickly.

Experiment 19.—Gold leaf introduced into the vapour of sulphur was apparently unchanged.

Experiment 20.—Thin sheet gold, thinner than that used for making the gold arsenide, was heated in a piece of combustion tubing for nearly an hour with the hottest flame obtainable with the blowpipe lamp used for making the experiments on gold and arsenic, but without fusing it or causing any signs of fusion to appear on its edges; hence there is no possibility of the gold having been fused in previous cases, *i.e.*, its fusion was due to the formation of a fusible compound with the arsenic. This test was repeated with the same result in both cases.

Experiment 21.—Some precipitated gold was made into an amalgam and roasted at a low temperature in the front part of a gas muffle. The gold was left as an ochre-coloured, lustreless, cauliflower-like mass; under the microscope, however, it is seen to have the usual colour and lustre of metallic gold; the innumerable bright points which reflect the light being too small to be seen by the unassisted eye, the general appearance is much like that of the excrescences of gold from roasted auriferous mispickel; but the spiral and moss-like growths are almost absent, although a number of hair-like filaments of gold are seen in the cavities and recesses of the mass.

When the pieces of amalgam were roasted at a high temperature they fused and coalesced; the appearance was rougher from the boiling and more rapid expulsion of the mercury, but the number of capillary growths and filaments was not increased. Doubtless most or all of the compounds of gold with volatile elements would yield moss gold on roasting.

Compounds of gold and arsenic do not appear to be mentioned in modern English works of reference upon chemistry. In Aitken's "Dictionary of Chemistry and Minerology," p. 537, London, 1807, there is an account of Hatchett's experiments upon them from *Phil. Trans.*, 1803, as follows:—

"If a small crucible containing gold be inserted in a larger one containing arsenic and an inverted crucible be luted on by way of a cover, and the apparatus be heated strongly in a wind furnace, the arsenic will be raised in vapour and the gold being fused in the arsenicated atmosphere, will combine with a small portion of it. The alloy hence resulting is of a grey colour, a coarse granular fracture, and very brittle.

"A heat equal to that of melting gold is by no means necessary to effect this combination, for if a plate of gold is merely brought to a full red heat in an atmosphere loaded with arsenic, the latter will unite superficially with the gold, and the alloy hence resulting, being very fusive, will trickle in drops from the plate, till the whole of it is thus arsenicated. The alloy is scarcely decomposable by mere heat, and at a high temperature the arsenic that is driven off carries a considerable proportion of gold with it."

An abstract of the above appears in Gmelin's "Handbook of Chemistry," vol. vi., p. 238, London, 1852, after which such compounds are ignored by more modern English writers, except a bare statement in "Watts's

Dictionary of Chemistry," vol. i., 1872, that gold combines with arsenic.

In Brough Smyth's "Gold Fields and Mineral Districts of Victoria," Melbourne, 1869, there is a statement that a quantity of arsenical gold was found by some Chinamen in the rubbish from disused roasting kilns at Stawell, in Victoria. This was examined by Mr. Newbery, who stated that the gold had probably taken up the arsenic (when the latter was in a state of vapour) during the roasting of arsenical ores, as native arsenides of gold were unknown in Victoria.

A. Deschamps (*Comptes Rendus*, lxxxvi., 1022-3 and 1065-6), states that Au_3As is formed as a dark red powder when metallic arsenic is placed in a solution of gold chloride. By fusion with potassium cyanide a yellow metallic button of Au_4As_3, sp. gr. 16·2, is obtained.

The above references were made after I had completed the experiments given in this paper, and they are quoted merely as of historical interest.

As a result of the foregoing experiments and observations I conclude that the peculiar form of the moss gold is due to the formation of a fusible compound with arsenic, which behaves in much the same way as fused bituminous coal—to which I referred in my first paper (*Jour. Roy. Soc. N.S.W.*, vol. x., 1876, p. 125) as follows:—"The general appearance of these peculiar cauliflower-like excrescences of gold would at first sight tend to give one the impression that they had been formed in somewhat the same way as the blebs and excrescences often observed on coke, which are so familiar to us in a fire made of the so-called bituminous coal, *i.e.*, caking coal, in which we constantly see portions of the coal fuse and swell up into fantastic blebs and bladders until the imprisoned gas breaks through the outer thin skin and inflames with a brilliant light. After the more combustible portions have been volatilised and consumed, a hard clinkery and more or less cauliflower-like excrescence is left." In the cavities of such cinder we may often see spicules and acicular threads of coke.

In that paper I came to the conclusion that the moss-like forms of gold could not be due to fusion, because the experiments were conducted at temperatures far below the fusing point of gold or mispickel, but my later investigations show that the moss gold is due to the fusion of the very fusible gold arsenide and to the escape of arsenic from it, blowing it up into excrescences, spicules, and spiral threads, and that the crystallised appearance in places is due to the ready crystallisation of the alloy on solidification.

In the auriferous mispickel the gold appears to be in the free condition, but to be converted into gold arsenide during the roasting, and it is from this gold arsenide that the moss gold is produced.

NOTICES OF BOOKS.

Manures and the Principles of Manuring. By C. M. Aitkin, B.Sc., F.R.S.E. Edinburgh and London: W. Blackwood and Sons. 1894. Small 8vo, pp. 592.

Dr. Aitkin is deservedly earning golden opinions for his contributions to the literature of agricultural chemistry. He enters upon his present task with a brief historical sketch of earlier views upon plant food. He mentions Helmont's notion that water alone supplied plants with all the materials for life and growth. He tells us that Sir Kenelm Digby (1669) traced vegetation to a balsamic saline juice, which is further explained to be "a nitrous salt dilated in the water," and he relates a number of experiments showing the nourishing effects of solutions of saltpetre applied to roses.

Next we come to the theory of Jethro Tull, of horse-hoeing celebrity. This experimentalist, once so famous, contended that plants were nourished by the particles of the soil itself, which if sufficiently comminuted rendered manures unnecessary, as well as the rotation of crops. The source of the carbon in vegetable tissues was first revealed by Bonnet, Priestley, and Sénébier.

The first book on the chemistry of agriculture published in the English language was Earl Dundonald's "Treatise showing the Intimate Connection that Exists between Agriculture and Chemistry" (1795). But his chemistry was misty and feeble. In 1804 Saussure made a more important contribution to the subject, showing the importance of the ash constituents of plants, and proving that their organic portion was mainly derived from water and from the carbonic acid of the air. Then came up the great problem of the source of the nitrogen in plants, a question which even yet has not been entirely decided.

Sir Humphry Davy's Lectures (1813) laid too much weight on the mechanical constitution of soils, and considered fertility as mainly due to them alone.

Boussingault (1834) took the epoch-making step of establishing a laboratory on a farm at Bechelbronn, in Alsace—in other words an "agricultural station."

The next great step was due to Liebig. He criticised the humus theory, and revived and extended the mineral theory of Saussure. But he erred in considering the mineral bases of plants as mutually replaceable. He first insisted on the value of nitrogen in manures, and then contended that it was unnecessary and that atmospheric ammonia was a sufficient source of combined nitrogen.

Recent observations, contrary to the theories of Pleasanton and others, show that not the blue but the yellow solar ray is most effective in decomposing the carbonic acid of the air. If such is the fact the possible value of the arc light, relatively so rich in the violet rays in promoting the growth of plants, will not be so great as it has been hoped.

As regards the nitrogen question it seems now demonstrated that leguminous plants at least can utilise the free nitrogen of the air by the intermediation of certain micro-organisms which exist in tubercles on the roots of peas, kidney-beans, &c. The experiments of Ville, however, seem to show that the power of fixing free nitrogen is not limited to the leguminous class.

Hampe, Wagner, and Wolff have also lately shown that organic nitrogen in the forms of urea, tyrosin, &c., can be assimilated by vegetation.

The humus theory, again, is being to a certain extent re-habilitated by recent inquiries. Humus is capable of enriching the soil with nitric nitrogen.

The chapter on the fertility of soils shows that it depends on physical, chemical, and biological properties acting in conjunction. Concerning the physical properties there is little difference of opinion. As regards chemical composition the author shows that the question is not so much the total amount of plant food in a soil as its availability.

The biological properties of soils are still not fully appreciated. Dr. Aikman divides the microbia of the soil into three classes, those which oxidise the ingredients of the soil, those which reduce, and those which fix nitrogen.

In considering the functions of manures the author considers nitrogen as "by far the most important." He shows that nitrogen is "essentially a superficial element." In soils the chief amount is found in the first nine inches. Peat soils are the richest, containing from 0·4 to 2·9 per cent, whilst marls contain from 0·004 to 0·083, and sands from 0·025 to 0·074. Schlœsing is quoted as considering that the chief source of atmospheric ammonia is the tropical ocean. The interesting remark is made that the bacteria which fix nitrogen in different plants belong to different species, a discovery which the author justly considers calculated to throw a new light on the principles of the rotation of crops.

A very serious question next considered is the loss of nitrogen due to a combination of causes, among which

the thorough drainage of the land takes a high rank. Our present mode of the disposal of sewage, for which we were as a nation solemnly execrated by Liebig, is still more prominent.

The most economical condition of the soil is pronounced to be permanent pasture. But though this treatment of the land may be the most economical from the mere point of view of the conservation of nitrogen, it is in other respects to be utterly condemned. It minimises the population which a country is able to maintain, and drives the inhabitants into the cities.

Dr. Aikman's view of farmyard manure is more favourable than that taken, *e.g.*, by Ville. It seems to us that he under-estimates the cost of its production. But he admits that as a supplier of the ingredients of plant food is grossly over-valued by the ordinary farmer, and that it contains the three capital elements nitrogen, phosphoric acid, and potash only in very small quantities. Here we may point out that, like most British agricultural chemists and unlike Ville, he does not place lime on an equality with the three elements just named; not, indeed, that it is less essential for most crops, but that it is abundantly present in most soils and is largely introduced by our phosphatic manures, superphosphates, bones, slag, guano, &c.

Guano is considered here as valuable from the complexity of its composition. It is found in practice preferable to mixtures of nitrates, sulphate of ammonia, and superphosphate. Its action is, in short, as the author declares, "one of many problems in manuring which illustrate how unsatisfactory is our knowledge of this most important department in agriculture."

On sewage manures the author's opinion is not favourable. His account of the A B C process errs by the statement that in it lime is used as one of the precipitating ingredients. On the contrary, the use of lime, except for neutralising acids present in industrial waste waters, is entirely excluded. Sewage sludge has been and still is produced in abundance which contains both nitrogen and phosphoric acid to the extent of about 3 per cent.

This admirable book, which we cannot examine at greater length, must not be supposed to contain instruction for compounding manures suitable for every soil and every crop. Nor does it profess to teach the analysis of manures, a subject which farmers and country gentlemen had better leave to professional hands. But all persons interested in agriculture will find themselves improved by a careful study of Dr. Aikman's work.

Pharmaceutical Journal of Australasia. Vol. vii., No. 1.

It is here mentioned, in an extract from the *Sud-Deut. Apotheker Zeitung*, that lupulin is spontaneously combustible.

Quackery in the Far East.—It is said that in Japan a nostrum bearing the title of the "Thousand Gold Medicine" is being hawked in all parts of the empire. It is made at Osaka, and is said to contain starch, catechu, thuja liquorice, elecamphane, camphor, and cloves.

Dangers of Soft Solder.—The impropriety of using soft solder in making up tinned goods, fruits, meats, &c., is emphatically pointed out. It is a ready cause of lead-poisoning.

Il Nuovo Cimento. Third Series, Vol. xxxv., February, 1894.

This journal was founded by Matteucci and Pina, continued by R. Felici, A. Battelli, and V. Volterra, and is now chiefly devoted to experimental physics and mathematics.

The present issue discusses electrolytic dissociation in connection with the optical rotatory power; the influence of magnetism and its mechanical action upon thermo-electric phenomena; the thermic phenomena of electrolysis; the relation between the electric conductivity and internal attrition of electrolytes on a case observed as regards influence of considerable masses of iron in the measurement of telluric magnetism, and on the unifilar magnetometer of Seni.

There are no papers on chemical subjects.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 11, March 12, 1894.

Preparation and Properties of Carbon Boride.—Henri Moissan.—This paper will be inserted in full.

The Use of Electricity to Follow the Phases of Certain Chemical Reactions.—Jules Garnier.—The author has executed certain experiments with the aim of utilising electricity to render account of the phases of certain metallurgical operations, measuring their duration and their intensity. He placed in a tube of refractory earth nickel oxide in powder mixed with wood charcoal. Two cylindrical bars of mild steel, penetrating into the tube at its two ends, compress the mixture between themselves, its thickness being a few c.m. This tube was laid horizontally in a small reverberatory furnace heated with coke, whilst the two steel bars were placed in the circuit of an electric current. At first the resistance opposed to the current was absolute; the ampèrage was null, but the voltmeter marked 50. After heating for fifteen minutes the needles got into movement, the ampèrage rose little by little, the voltage declined, so that at a given moment he had nearly 50 ampères and scarcely any resistance. After a moment of equilibrium in this position, the needles of the ampères and the volts returned by degrees to their original position, and became fixed at 45 volts and 1 or 2 ampères. These progressive variations in the electric current, first in one direction and then in the other, indicate the reactions effected in the mixture of oxide and charcoal. In another experiment the author operated on a mixture of copper, nickel, and iron oxides. Notwithstanding the complexity of the mixture, the successive phases of the reduction of the three metals were well indicated by the variations in the intensity of the electric current. Thus the manager of a metallurgical works, without leaving his office, may follow by the needles of the ammeters and voltmeters the phases of the manufacture of steel on the sole, or of the refining of a bath of copper or other metals.

A Contribution to the Study of Yeast.—P. Hautefeuille and A. Perry.—The authors classify the ferments of the Burgundy vineyards in three groups. Those of the first class are apiculated; those of the third group are ellipsoidal.

The Spark Spectra of Certain Minerals (Metallic Sulphides).—A. de Grammont.—This paper will be inserted in full.

Journal fur Praktische Chemie.
Vol. xlix., No. 1, January 4, 1894.

On Isoborneol.—J. Bertram and H. Walbaum.—The authors describe the preparation and properties of isoborneol. It crystallises out of petroleum ether in thin, feathery leaflets; it is readily soluble in alcohol, ether, chloroform, and benzene, but insoluble in water. Its composition is $C_{10}H_{18}O$. If allowed to stand for some time along with a molecular proportion of phenylisocyanate, it forms isobornylphenylurethan. Isoborneol combines with

bromal and chloral. The authors have examined the formic and the acetic esters, its ethers, and its oxidation products.

Occurrence of Camphene in Ethereal Oils.—J. Bertram and H. Walbaum.—The authors have obtained camphene from the oils of citronella, of ginger, and of camphor.

Addition of Sodium Acetacetic Ether and Sodium Malonic Ether to the Ethers of Non-saturated Acids.—A. Michael.—The fourth part of a voluminous paper.

Contributions to a Knowledge of the Formation of Rings in Organic Nitrogenous Compounds.—A. Michael.—This paper is too extensive for insertion, and does not admit of useful adridgement.

Refrigerators for Laboratories.—Dr. J. Walter.—This paper requires the two accompanying figures.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxv., No. 1, January, 1894.

On Carborundum.—G. Deprez.—The author mentions certain artificial substances rivalling the hardness of the diamond: 1. Crystalline boron, obtained by a costly process. 2. Moissan's artificial diamond, which has not yet been produced in a practical manner. 3. The product obtained by Schützenberger in his researches on the compounds of carbon and silicon. It contains 70 per cent of silicon and 30 per cent of carbon. It is obtained by passing an electric current through a mixture of coke, 45½ per cent; sand, 36½ per cent; and common salt, 18 per cent. The process is conducted in a furnace.

Use of Calcium Plumbate in the Manufacture of Glass.—Dr. G. Kassner.—This compound is obtained by igniting sand, 100 kilos.; felspar, 25 kilos.; soda, 35; red lead, 15; and lime-stone, 17·5 kilos. The compound obtained is in the state of powder, and consequently does not require grinding when mixed with the other materials.

MISCELLANEOUS.

Indol as a Reagent for Nitrites.—Prof. Odo Bujwid (*Chemiker Zeitung*).—A very sensitive and beautiful reaction for traces of nitrites in the examination of water is obtained with indol. An alcoholic solution at 0·1 to 0·2 part per 1600 is diluted with water. The author takes 10 c.c. of water, heats it to 70°—80° along with a few drops of hydrochloric acid (free from nitrites), and adds a few drops of the solution of indol. There at once appears a fine red colour, which becomes rather deeper for a few minutes. The reaction can be applied colorimetrically.

Royal Institution of Great Britain.—*Friday Evening Meetings after Easter*, 1894.—April 6, Professor Victor Horsley, M.B., B.S., F.R.C.S., F.R.S., "Destructive Effects of Projectiles." April 13, Professor J. J. Thomson, M.A., Sc.D., F.R.S., "Some Properties of the Electric Discharge through Gases." April 20, John G. Garson, M.D., "Early British Races." April 27, Professor H. Marshall Ward, D.Sc., F.R.S., F.L.S., "Action of Light on Bacteria and Fungi." May 4, German Sims Woodhead, M.D., "Spread of Tuberculosis by Food." May 11, The Rev. S. Baring-Gould, M.A., "English Folk Song" (with musical illustrations). May 18, Professor A. M. Worthington, M.A., F.R.S., "The Splash of a Drop and Allied Phenomena." May 25, Sir Howard Grubb, F.R.S., F.R.A.S., "The Development of the Astronomical Telescope." June 1, Professor Oliver Lodge, D.Sc., LL.D., F.R.S., "The Work of Hertz." June 8, C. Vernon Boys, F.R.S., A.R.S.M., "The Newtonian Constant of Gravitation."

The Paris Water Supply.—M. Bucquoy has informed the Academy of Medicine that the present epidemic of typhoid fever is due to the drinking-water, which contains 15,000 micro-organisms per c.c.

Absorption-Spectrum of Solutions of some Chromium Oxalates of the Blue Series.—G. Magnanini and T. Bentivoglio (*Atti d. Reale Accademia dei Lincei*).—The chromium oxalates of potassium, sodium, and ammonium, the dilute solutions of which possess, according to Ostwald, the same absorptive power for light, display the same behaviour in very concentrated solutions (20 to 25 per cent), in which their dissociation into R_3 and $Cr(C_2O_4)_3$ is by no means complete. If such a solution of sodium chrome-oxalate is mixed with sodium nitrate, and thereby the degree of dissociation of the former salt is decreased, the absorptive power of the solution for light is not altered. If, on the contrary, the solution of that salt is diluted, the coefficients of exertion remain proportional to the concentration of the solution. Hence it follows that in the solutions of the salts in question the power of absorbing light is perfectly independent of the degree of their electrolytic dissociation.

Proportion of Plant Food in Fæcal Matter.—Adalbert von Podowils (*Chemiker Zeitung*).—The author has closely examined the manurial value of fæces both on the small and the large scale. He finds that the value of fæces, when recent and when a year old, is practically alike, the chief difference being that when recent they contain their nitrogen in organic combinations, and when rotted in the state of ammoniacal salts. The common assumption that the fæces contain yearly per head 5 kilos. nitrogen, 1·3 kilos. phosphoric acid, and 1 kilo. potassa, the author finds excessive. The utmost quantity really attainable he takes at per head yearly, 2·12 kilos. nitrogen, 0·92 kilo. phosphoric acid, and 0·84 kilo. potassa. If we assume that 20 per cent of the excreta find their way into fields and public urinals, and that a further 10 per cent nitrogen are lost by evaporation, the real quantity produced per head yearly will be 3·03 kilos. nitrogen, 1·15 kilos. phosphoric acid, and 1·05 kilos. potassa.

Elizabeth Thompson Science Fund.—This fund, which has been established by Mrs. Elizabeth Thompson, of Stamford, Connecticut, "for the advancement and prosecution of scientific research in its broadest sense," now amounts to 26,000 dollars. As accumulated income will be available June next, the trustees desire to receive applications for appropriations in aid of scientific work. This endowment is not for the benefit of any one department of science, but it is the intention of the trustees to give the preference to those investigations *which cannot otherwise be provided for*, which have for their object the advancement of human knowledge or the benefit of mankind in general, rather than to researches directed to the solution of questions of merely local importance. Applications for assistance from this fund, in order to receive consideration, *must be accompanied by full information*, especially in regard to the following points:—1. Precise amount required. Applicants are reminded that one dollar ($1.00) is approximately equivalent to four English shillings, four German marks, five French francs, or five Italian lire. 2. Exact nature of the investigation proposed. 3. Conditions under which the research is to be prosecuted. 4. Manner in which the appropriation asked for is to be expended. All applications should reach, before June 1, 1894, the Secretary of the Board of Trustees, Dr. C. S. Minot, Harvard Medical School, Boston, Mass., U.S.A. It is intended to make new grants in June, 1894. The trustees are disinclined, for the present, to make any grant exceeding three hundred dollars; decided preference will be given to applications for smaller amounts.—(Signed) HENRY P. BOWDITCH, President: WILLIAM MINOT, Jun., Treasurer; EDWARD C. PICKERING; FRANCIS A. WALKER; CHARLES-SEDWICK MINOT, Secretary,

MEETINGS FOR THE WEEK.

MONDAY, 2nd.—Society of Arts, 8. (Cantor Lectures). "Photometry," by Capt. W. de W. Abney, C.B., F.R.S.
—— Royal Institution, 5. General Monthly Meeting.
—— Medical, 8.30.
TUESDAY, 3rd.—Royal Institution, 3. "Electric Illumination," by Prof. J. A. Fleming.
—— Institute of Civil Engineers. 8.
—— Pathological, 8.30.
WEDNESDAY, 4th.—Society of Arts, 8. "The Elements of Beauty in Ceramics," by C. F. Binns.
THURSDAY, 5th.—Royal Institution, 3. "The Etching Revival," by F. Seymour Haden.
FRIDAY, 6th.—Royal Institution, 9. "Destructive Effects of Projectiles," by Prof. V. Horsley.
—— Geologists' Association, 8.
—— Quekett Club, 8.
SATURDAY, 7th.—Royal Institution, 3. "Life among the Afghans," by J. A. Gray.

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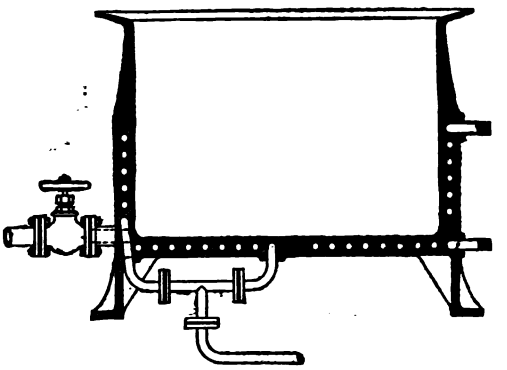

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says;—
P. 316. "An improved vessel for boiling oil, and suitable for many other kindred purposes, has been recently described by T. Frederking (CHEMICAL NEWS, London). A coil of stout piping is arranged in a casting mould, so that the molten metal forming the pan is cast round the coil, much as is done in the case of the water-tuyeres of a blast furnace. Steam at any pressure [or any other heating medium] being passed through the coil, the pan is heated up proportionately without any danger, the pressure bearing solely on the piping and not on the metal pan itself, whilst the well conducting metal walls allow the heat to pass readily. Temperatures up to 350° and 400° C. can be thus obtained."
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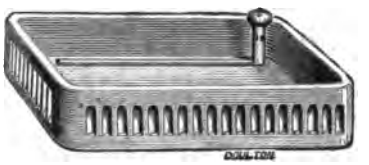

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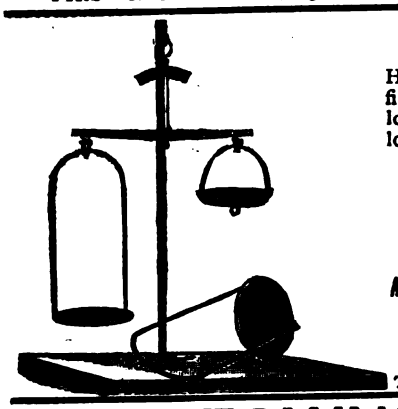

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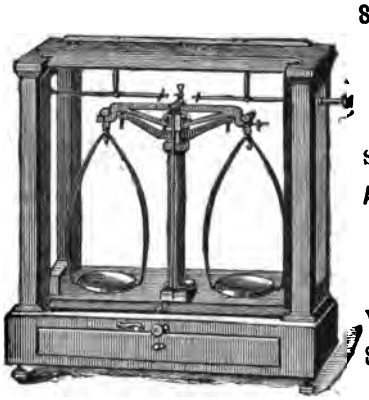

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EFFECT OF CARBON DIOXIDE, CARBONIC OXIDE, SULPHURETTED HYDROGEN, AND WATER- AND COAL-GAS ON ANIMAL LIFE.*

By JOSEPH R. WILSON.

SINCE the health of every individual is dependent upon the purity of the atmosphere, a knowledge of the effect of impurities in the air on animal life is of the highest importance to the community at large, but of special importance to those who work in coal, silver, lead, copper, or gold mines, or at iron furnaces, coke ovens, &c., where impurities often exist, such as—

	S. D.
CO_2, choke damp or carbon dioxide	1·529
CO, white damp or carbonic oxide	0·9678
H_2S, sulphuretted hydrogen or hydrogen sulphide	0·1912

The statistics compiled by me from the Indices of the Library of the College of Physicians, Philadelphia, one of the most complete institutions in the world, show that 90 per cent of the total scientific experiments on the effects of noxious gases on animal life have been made by the Germans and French, and for the last decade scarcely any experiments have been made in this direction by scientists of any nationality, the results obtained by our forefathers being accepted with a credulity seldom encountered in other brances of science. In addition to this, the poverty of information in the standard references on this subject is so great, that were any particular knowledge required, it would be necessary to make new experiments to determine the same. With these facts before me, in grouping the results obtained in experiments with carbon dioxide, carbonic oxide, and sulphuretted hydrogen on animal life, the medical fraternity will at least have a condensation of experiments for reference, from many authorities combined with the results of my own experiments. I claim that my experiments are absolutely accurate, as the means employed for mixing the different atmospheres (the Shaw gas-tester) is acknowledged to be as nearly perfect as human agency can make anything, and has been awarded the Elliott Cresson and Scott Legacy Medals for accuracy—the highest awards in the gift of the Franklin Institute, and is to gases what weights and scales are to solids.

It is not my intention to go into the constituents of the above gases, there being no necessity for my doing so in this paper. I have simply one object in view, to describe the effect produced by them on animal life, the result of recent experiments. The Shaw gas-tester, which I used for mixing my gases in the centesimal proportions desired, is an apparatus simple, convenient, and accurate, consisting of two pumps with pistons attached to a graduated arm, so that one cylinder can be set to pump 10 per cent of gas and the other 90 per cent of air—or *vice versâ*; or any per cent, to the lowest fraction. It is the only instrument in the world capable of mixing gases accurately, rapidly, and continuously in any per cent desired, the product of the two cylinders being forced through an ejector or mixer before delivery.

The animal under treatment is placed in a bell-shaped glass cylinder 16 inches high, 4 inches diameter at neck, and 8 inches at base. The cylinder is placed horizontally on the table, with the neck towards the operator, and is connected with the instrument, at the neck, by means of a rubber tube. The animal rests on all fours facing the operator, with its nose near the aperture through which the gases enter to the cylinder from the instrument or mixer.

The end of the bell-shaped glass cylinder is entirely open to the air, so that the mixture of gas and air is discharged and replaced every four seconds by each stroke of the pump, always maintaining a constant mixture, preventing stratification, or contamination through the exhalations of the subject. The cylinder being of glass and perfectly transparent, enables the operator to observe every change in the condition of the animal.

The difference in results obtained by the various authorities has caused me to make the following experiments to satisfy myself, an accurate knowledge on this subject being necessary to the pursuit of my profession, and I am well aware of the great difficulties experienced by my predecessors in making accurate mixtures of gases, owing to the crude appliances at their command for this purpose.

As a prelude to my experiments I will give the results obtained with carbon dioxide by scientists whom we are accustomed to quote:—

Carbon Dioxide.

J. H. Merrivale says it extinguishes lights and is fatal to animal life.

	Per cent.
J. J. Atkinson says dangerous to life	8
lights extinguished ..	10
Fairley's "Catechism"—dangerous to life	3
will cause death quickly	10
lights will burn in	10 to 20
Sir H. Roscoe's "Chemistry"—will not support combustion of candle	3 to 6
Dr. A. Smith—lights extinguished, about ..	2
would suffocate	4

"Watts's Dictionary of Chemistry" says:—"Animals immersed in it soon die, not for want of oxygen, but in consequence of a direct poisonous action, violent spasms being sometimes produced; sometimes complete atony of the cerebral faculties."

"Ency. Brit.," vol. v., p. 87, says:—"Will not burn; neither does it support combustion."

Dr. Karl Friedlander, of Berlin, in experiments on animal life, states that 62·8 per cent killed a rabbit in twenty-seven minutes; 65 per cent killed a rabbit in forty-five minutes; the higher per cent in this instance taking longer to kill the rabbit than the lower per cent, showing a wide variation in his tests, which I can only account for in the imperfect appliances at his command for placing definite quantities of gas in the atmosphere and maintaining a constant mixture of definite proportions. Rabbits, like human beings, have their ailments, and I have found in the course of my experiments that disease in the shape of a fatty accumulation about the heart disqualifies the animal entirely for tests of this nature, death resulting in one-tenth of the time necessary to produce the same result on a perfectly healthy animal, but in the above instance the difference in time of immersion in such a high per cent is not great enough for me to ascribe the difference in effect to any organic disease, but rather to the imperfect mixing of the gases.

In all my experiments I have found that the smaller the animal the sooner it succumbed to poisonous gases. My first experiments were made with small birds, then I tried mice, after which I bestowed my attention on guinea pigs, finally selecting the rabbit as a base for the experiments which I now present.

Effects of Carbon Dioxide on Animal Life.

No. 1.—I placed a rabbit in a glass cylinder and pumped

* A Lecture delivered before the Philadelphia College of Pharmacy, November 21, 1893. From the *American Journal of Pharmacy*, lxv., No. 12.

in an atmosphere of 10 per cent of CO_2 and 90 per cent of air.

After one hour and seven minutes the rabbit gave no indication whatever of being affected, so I released it and allowed it to run with several others of its species; the effect of its treatment, contrary to expectation, was great exhilaration, instead of stupefaction.

Result.—10 per cent CO_2 and 90 per cent air, one hour seven minutes inhalation; exhilaration.

No. 2.—I placed a rabbit in a glass cylinder and pumped in an atmosphere of 25 per cent of CO_2 and 75 per cent of air for one hour, at the end of which time the animal showed no indication whatever of being affected, and when released and placed with the others exhibited as much liveliness as any of them.

Result.—25 per cent CO_2 and 75 per cent air, one hour inhalation; unaffected.

No. 3.—I placed a rabbit in a glass cylinder and pumped in an atmosphere of 50 per cent of CO_2 and 50 per cent of air. At the end of two minutes the rabbit showed signs of being affected. At the end of three minutes the rabbit commenced to gasp regularly every two seconds.

At the end of	6	minutes	gasps were	3	seconds apart.
"	10	"	"	4	"
"	12	"	"	6	"
"	14	"	"	8	"
"	15	"	"	9	"
"	16	"	"	10	"
"	17	"	death ensued.		

Result.—50 per cent CO_2 and 50 per cent air, seventeen minutes inhalation; death.

No. 4.—I placed a rabbit in a glass cylinder and pumped in an atmosphere of 75 per cent of CO_2 and 25 per cent of air.

At the end of	2	minutes	rabbit commenced to pant rapidly.		
"	3	"	it became stupefied and gasped every two seconds.		
"	5	"	gasps were every	3	seconds apart
"	7	"	"	5	"
"	8	"	"	6	"
"	9	"	"	10	"
"	10	"	death ensued.		

Result.—75 per cent CO_2 and 25 per cent air, ten minutes inhalation; death.

No. 5.—I placed a mouse in a glass cylinder and pumped in an atmosphere of pure CO_2; death was instantaneous.

Result.—Pure CO_2; death instantaneous (mouse).

No. 6.—I placed a mouse in a glass cylinder and pumped in an atmosphere of 25 per cent CO_2 and 75 per cent of air. At end of three minutes mouse seemed slightly affected but kept moving around the cylinder, in this test held vertically. At the end of ten minutes conditions were unchanged, so I displaced the atmosphere of 25 per cent CO_2 with pure air.

Result.—The mouse revived, instantaneously on first inhalation.

Result.—25 per cent CO_2 and 75 per cent air, ten minutes inhalation, slightly affected but recovered instantaneously in fresh air (mouse).

No. 7.—I placed a mouse in a glass cylinder and pumped in an atmosphere of 50 per cent of CO_2 and 50 per cent of air.

At the end of	10	seconds	mouse showed great exhilaration.
"	20	"	its activity was greatly reduced.
"	30	"	it became stupefied.
"	35		gave short gasps.
"	45		gasps were long and apparently painful.
"	55		death occurred.

Result.—50 per cent CO_2 and 50 per cent air, fifty-five seconds inhalation; death (mouse).

Experiments 5, 6, and 7 are only given here to illustrate the fact that the smaller the animal the less the power of resistance against CO_2.

Carbonic Oxide, CO.

The results obtained by scientists whom we are accustomed to quote, on the effect of carbonic oxide on animal life, are first epitomised.

H. Letheby, M.B., B.A., Ph.D., &c., late Professor of Chemistry and Toxicology in the Medical College of the London Hospital, says that 5 per cent of CO killed small birds in three minutes; one per cent in half that time; 2 per cent will render guinea pigs insensible in two minutes. In all cases effects were the same. The animals show no signs of pain, they fall insensible, and either die at once with a slight flutter, hardly amounting to a convulsion, or gradually sleep away as if in a profound slumber.

Post-mortem.—Blood a little redder than usual.

Prof. A. R. Leeds says:—"The operation of pure CO is so immediate as to prevent the lungs throwing off a single charge received."

"Watts's Dictionary of Chemistry" says:—"It is a very poisonous gas, acting chiefly on the nervous system, causing giddiness when inhaled; sometimes acute pain in various parts of the body, and after a while complete asphyxia."

Buck, on Hygiene and Public Health, says:—"It is not so immediately fatal as carbonic acid gas."

"Ency Brit.," vol. v., p. 87, says:—"It is an extremely poisonous gas, being capable of displacing the oxygen in the blood, owing to a compound with the hæmoglobin, with which the oxygen is ordinarily combined."

"American Ency.," vol. iii., p. 775, says:—"It is more irrespirable and poisonous than carbon dioxide. Its inhalation from furnaces sometimes causes immediate asphyxia to the workmen."

I will now submit results of my own experiments on the effect of carbonic oxide on animal life, but have to omit several important tests, owing to the carelessness of a servant in destroying my notes.

No. 1.—I placed a rabbit in a glass cylinder and pumped in an atmosphere of 2 per cent of CO and 98 per cent of air. At the end of ten minutes the posterior extremity of the rabbit became paralysed; at the end of eighteen minutes forelegs became paralysed, and at the end of twenty minutes the rabbit became semi-comatose; at the end of forty-five minutes condition had not altered; on being placed in the fresh air it revived sufficiently to maintain its equilibrium.

Result.—2 per cent CO and 98 per cent air, revived in fresh air after forty-five minutes inhalation of the gas.

No. 2.—I placed a rabbit in a glass cylinder and pumped in an atmosphere of 2·5 per cent of CO and 97·5 per cent air. At the end of five minutes the rabbit became semi-comatose, but on being placed in pure air recovered almost immediately.

Result.—2·5 per cent CO and 97·5 per cent air, revived in fresh air after five minutes inhalation of the gas.

No. 3.—I placed a rabbit in a glass cylinder and pumped in an atmosphere of 4 per cent of CO and 96 per cent of air. Death resulted in four and a half minutes.

Result.—4 per cent CO and 96 per cent air, four and a half minutes inhalation; death.

No. 4.—I placed a mouse in a glass cylinder and pumped in an atmosphere of 0·2 of 1 per cent CO. At the end of six minutes the mouse showed no signs whatever of being affected.

No. 5.—Increased the atmosphere to 0·5 of 1 per cent of CO. At the end of five minutes the mouse showed no signs whatever of being affected.

No. 6.—Increased the atmosphere to 1·0 per cent of CO. At the end of thirty minutes the mouse showed no signs of being affected. Gave it then fresh air to revive it for one minute. Increased atmosphere to 2·0 per cent CO. Mouse died in ten minutes; death accompanied with a total relaxation of all the muscles.

Result.—2 per cent CO and 98 per cent air, ten minutes inhalation; death (mouse).

No. 7.—I placed a mouse in an atmosphere of 2·5 per cent of CO and 97·5 per cent air; mouse died in five minutes.

Result.—2·5 per cent CO and 97·5 per cent air, five minutes inhalation; death (mouse).

No. 8.—I placed a mouse in an atmosphere of 10 per cent of CO, 90 per cent air; death resulted in three minutes.

Result.—10 per cent CO and 90 per cent air, three minutes inhalation; death (mouse),

In the absence of the missing tests I have included experiments 4, 5, 6, 7, and 8 simply to illustrate the fact that the smaller the animal the less the power of resistance against CO.

Sulphuretted Hydrogen.

I note again the results obtained by scientific authorities whom we are accustomed to quote, on the effect of *sulphuretted hydrogen* on animal life:—

"Watts's Dictionary of Chemistry," p. 203, says:—"An atmosphere of one-tenth of 1 per cent of this gas proves fatal to lower animals."

Extract from "Public Health Reports and Papers," vol. iii., pp. 75, 76, says:—"It is poisonous and its action on arterial blood is a common lecture table experiment."

"Ency. Brit., Chemistry," vol. v., p. 500, says:—"It cannot be breathed with impunity, frequently giving rise to nausea and vertigo, even when much diluted."

"American Ency.," vol. ix., p. 130, says:—"Theuard found that a small bird would die in air containing fifteen one-hundredths of 1 per cent, and a horse in air that contained $\frac{1}{2}$ of 1 per cent."

The results of my experiments on the effect of H_2S on animal life are as follows:—

No. 1.

1. I placed a rabbit in a glass cylinder and pumped in an atmosphere of 1 per cent of H_2S and 99 per cent of air.

2. I placed another rabbit, in another glass cylinder and pumped in an atmosphere of 1 per cent of H_2S, and 99 per cent of air simultaneously with the No. 1, using two Shaw gas testers as mixers for the operation, both connected with the same bag of H_2S.

Death occurred simultaneously in cylinders Nos. 1 and 2, at the end of one minute, preceded by violent convulsions which lasted about ten seconds.

Result.—1 per cent H_2S and 99 per cent of air, one minute inhalation; death.

No. 2.

1. I placed a rabbit in glass cylinder No. 1, and pumped an atmosphere of 0·5 of 1 per cent of H_2S and 99·5 per cent of air.

2. I placed another rabbit in glass cylinder No. 2, and pumped in an atmosphere of 0·5 of 1 per cent of H_2S and 99·5 per cent of air, simultaneously with No. 1, using two Shaw gas testers as mixers for the operation, both connected with the same bag of H_2S. Death occurred simultaneously in cylinders 1 and 2, at the end of three minutes, preceded by violent convulsions which lasted about fifteen seconds.

Result.—0·5 of 1 per cent H_2S and 99·5 per cent. air, three minutes inhalation; death.

No. 3.

1. I placed a rabbit in glass cylinder No. 1, and pumped in an atmosphere of 0·2 of 1 per cent of H_2S, and 99·8 per cent of air.

2. I placed another rabbit in glass cylinder No. 2, and pumped in an atmosphere of 0·2 of 1 per cent of H_2S, and 99·8 per cent of air, simultaneously with No. 1, using two Shaw gas testers as mixers for the operation, both connected with the same bag of H_2S. Death resulted simultaneously in cylinders Nos. 1 and 2 at the end of ten minutes.

Result.—0·2 of 1 per cent H_2S, and 99·8 per cent air, ten minutes inhalation; death.

No. 4.—I placed a rabbit in a glass cylinder and pumped in an atmosphere of one-tenth of 1 per cent of H_2S, or the $\frac{1}{1000}$ part and 99·9 per cent of air. Death resulted in thirty-seven minutes.

Result.—0·1 of 1 per cent H_2S or the $\frac{1}{1000}$ part, and 99·9 per cent of air, thirty-seven minutes inhalation; death.

Note.—In all of the above tests rabbits were seized with convulsions ten to fifteen seconds after immersion in poisonous atmosphere, which lasted on an average about twelve seconds.

No. 5.—I placed a rabbit in a glass cylinder and pumped in an atmosphere of $\frac{2}{1000}$ of 1 per cent of H_2S, and 99 and $\frac{998}{1000}$ per cent of air. At the end of two hours, rabbit showed no signs whatever of being affected, so I released it.

Result.—$\frac{2}{1000}$ of 1 per cent of H_2S, and 99 and $\frac{998}{1000}$ of air, after two hours inhalation; unaffected.

Effect of Illuminating or Coal and Water Gas on Animal Life.

The frequent occurrence of accidental deaths from illuminating gas has caused me to make a series of experiments on this subject with a view to determining just how much risk we run in having a small escape of gas in our bed-rooms, for instance, and the results obtained ought to act as a warning to all who are anyway careless in turning off the stop-cocks before retiring, or who carelessly turn the gas low near a draft and find it blown out the next morning and the room filled with gas.

No. 1.—I placed a rabbit in a glass cylinder and pumped in an atmosphere of 75 per cent of illuminating gas (water and coal gas) and 25 per cent of air. Rabbit was immediately seized with violent convulsions and death ensued in two minutes.

Result.—75 per cent illuminating (water and coal gas) and 25 per cent air, two minutes inhalation; death.

No. 2.—I placed a rabbit in a glass cylinder and pumped in 25 per cent of illuminating gas (water and coal gas) and 75 per cent air; on the third inhalation the rabbit was seized with violent convulsions and urinated freely; at the end of one minute convulsions ceased, and at the end of four minutes death ensued.

Result.—25 per cent illuminating gas (water and coal gas) and 75 per cent air, four minutes inhalation; death.

No. 3.—I placed a rabbit in a glass cylinder and pumped in 15 per cent of illuminating gas (water and coal gas) and 85 per cent of air; without any struggling it sank into a comatose state; at the end of three minutes it struggled feebly; at the end of four minutes urinated; and at the end of six minutes death ensued.

Result.—15 per cent illuminating gas (water and coal gas) and 85 per cent of air; six minutes inhalation; death.

No. 4.—I placed a rabbit in a glass cylinder and pumped in 10 per cent of illuminating (water and coal) gas and 90 per cent. of air; at the end of thirteen minutes rabbit was seized with convulsions and died in five seconds.

Result.—10 per cent illuminating (water and coal) gas and 90 per cent. air; thirteen minutes inhalation; death.

No. 5.—I placed a rabbit in a glass cylinder and pumped in an atmosphere of 5 per cent of illuminating (water and coal) gas and 95 per cent. of air. At the end of ten minutes rabbit was seized with strong convulsions which lasted twenty seconds; at the end of twenty minutes rabbit commenced to gasp; and at the end of thirty minutes death ensued.

Result.—5 per cent illuminating (water and coal) gas and 95 per cent of air; thirty minutes inhalation; death.

I did not analyse the illuminating gas for its constituents, but the gas used was Philadelphia city gas, and I believe it contains about 30 per cent CO.

I have other experiments on hand on CH_4, carburetted

hydrogen or fire damp, also the effect of carbon dioxide or choke damp on lights, the results of which it will afford me pleasure to make known in a future paper.

ON THE CONDITION OF GOLD IN QUARTZ AND CALCITE VEINS.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

The condition in which gold occurs in veins and other matrices has long been a matter of interest to me, and from time to time I have made occasional experiments, as opportunity offered between other duties, to ascertain whether the gold scattered through quartz veins and other gangues is crystallised or not.

When the gold occurs in a soft matrix like calcite or serpentine it very often is crystallised, so also when it occurs in cavities, such as those left by the removal of iron pyrites, but it is rather difficult at times to decide whether gold present in a hard matrix is or is not crystallised. To answer the question one cannot crush the specimen under a hammer or in a mortar, because this treatment would destroy the form of the gold as well as remove the enclosing matrix.

In order to remove the gangue, usually quartz, the auriferous specimens were placed in the form of fragments, as large as possible, in a platinum crucible or dish according to size and condition, and acted upon by the ordinary solution of hydrofluoric acid, until all the quartz or gangue was either removed, or so much disintegrated as to be easily removed or washed away from the gold.

A piece of the porous white siliceous matrix resembling geyserite from Mount Morgan was attacked by hydrofluoric acid, but only one speck of gold was left, and that was not visible until after the residue from the mineral had been crushed in an agate mortar.

On treating the stalactites of auriferous brown hæmatite from Mount Morgan with hydrochloric acid, as described in a paper read before the Royal Society of New South Wales, December 2, 1891 ("On some New South Wales and other Minerals," Note No. 6), a residue of silica was left. In some cases the residue consisted of gelatinous silica, in others of porous quartz resembling the so-called geyserite, although before such treatment in most cases no quartz was visible, nor was there anything to indicate its presence; the original colour of the stalactites being dark brown to lustrous black, as in the typical brown hæmatite, neither did the fracture reveal the presence of silica.

As the solution went on and the iron oxide was removed, the stalactites gradually presented an outline in soft transparent gelatinous silica; this increases until finally nothing but gelatinous silica, or a mixture of it and ordinary silica, was left. No gold was visible in the residue, either in the first or second sample tried, even after crushing the residue in an agate mortar.

In a third specimen the silica also was got rid of by hydrofluoric acid; on grinding the residue, mainly insoluble iron oxide, in an agate mortar, no traces of gold could be seen. This appears to indicate that the particular specimens were either free from gold, most unlikely, or that owing to its finely-divided condition it had floated away during the treatment.

When acted upon by hydrofluoric acid the stalactitic brown hæmatite soon acquired a white appearance, and the various fragments became more or less cemented together into rounded masses, with numerous vent holes, through which the volatile silicon fluoride, acid, and steam escaped, so that they looked like many a New Zealand Hot Spring in miniature. The quartz is rendered soft and friable long before it is removed by the hydrofluoric acid.

A fourth specimen left a residue of very finely-divided gold, but without any recognisable crystalline form. A fifth specimen left the gold as a dull brown powder.

A rich specimen of gold quartz from New Caledonia Reef, Queensland, was treated in the same way, when a considerable amount of dull brown gold was left; but with no traces of crystallisation.

A specimen of quartz from Armageddon Reef, Gilbert River, Queensland, showing "spider leg" gold, was treated with hydrofluoric acid to remove the quartz; the gold set free was seen to consist of striated wire-like forms and of cavernous octahedrons joined together into chains.

An exceedingly rich specimen of water-worn quartz and gold, containing more gold than quartz, which was thought might show the gold crystallised, was next treated, but after removal of the quartz, the gold, although presenting a very bright and lustrous appearance, did not show any recognisable crystalline form; it and the quartz had apparently solidified together and neither had been free to crystallise. Several other specimens were examined, but in none was any distinct crystalline form recognisable,

The gold set free from vein quartz by hydrofluoric acid shows no sign of fusion (the old theory that the quartz of veins had originally been in a molten condition and had been ejected from below into fissures is, of course, nowadays no longer held), neither does it as a rule show any well-marked cavities or in other favourable condition for assuming such forms.

It usually presents the appearance of irregular films, plates, threads, and masses which are more or less connected together, sometimes so closely that when the quartz is wholly removed, a rough spongy or cavernous mass of gold is left, retaining more or less completely the outlines possessed by the fragment of auriferous quartz before it was acted upon by the acid.

A specimen of the auriferous mispickel in calcite, from Lucknow, weighing about three ounces, was treated with hydrochloric acid to dissolve away the calcite; the residue consisted of mispickel, quartz, and a white asbestiform mineral—the latter was not previously visible; in addition to the more massive pieces, thin plates of mispickel were left, and these had apparently surrounded crystals of calcite, since some of them were arranged so as to form hollow rhombohedrons; some of the rhombohedrons were cut in half by diagonal films of mispickel.

On treating these plates with nitric acid to see if they contained any free gold, they were in some cases found to consist of quartz merely coated with mispickel. In this instance no free gold was left, neither by the calcite nor by the mispickel.

Another piece of the auriferous mispickel in calcite from Lucknow was roasted and yielded large excrescences of moss gold; this was removed and the residue of iron oxide, lime, silica, and undecomposed mispickel, was treated with hydrochloric acid until only some silica and a little gold were left. The gold was very finely divided and floated readily on water, but appeared as if somewhat crystallised.

The calcite from another specimen, but unroasted, was removed by hydrochloric acid, and a small amount of fine free gold was left, together with some powdery mispickel and silica which had been enclosed within the calcite—under the microscope the gold was seen to be more or less crystallised.

In the rich gold calcite specimens from the above and other New South Wales mines, as well as those from Gympie, Queensland, the gold can be seen to be crystallised, so also in the serpentine from Gundagai and Lucknow, and some of the clear auriferous quartz from New Zealand, but in the majority of cases, for I have only quoted a few out of numerous trials, the gold embedded in massive quartz is remarkably free from any traces of crystalline form, and the larger the fragments of gold the less crystalline form does it present.

* A Paper read before the Royal Society of New South Wales.

A splinter of gold with octahedral faces on both ends, enclosed in a small rock crystal is stated by Selwyn and Ulrich ("Phys. Geog. Geol. and Mineralogy of Victoria," 1866, p. 43) to have been obtained from the M'Ivor Gold Field, together with other crystallised specimens of quartz containing non-crystallised gold.

Crystallised gold is not usually met with in the quartz of the reef itself, but in the upper portions of the ferruginous and argillaceous casing of the reef and in the detritus near its outcrop.

Some alluvial gold which I obtained on the spot at Fairfield, New England, N.S.W., was examined; on removing the fine sand from this by washing, the gold under the microscope did not look water-worn but obscurely crystallised, a more or less complete octahedral face being occasionally seen. The gold was obtained from a spot close to the reef, and had evidently not travelled many feet.

The really good crystals of gold all appear to have formed in what are now cavities, usually left by the removal of iron pyrites, or else in very soft matrices, like iron oxides, clay, calcite, and serpentine, as already mentioned.

THE QUESTION OF THE OCCURRENCE OF HYDROGEN PEROXIDE IN ATMOSPHERIC AIR AND IN ATMOSPHERIC WATERS.*

By EM. SCHÖNE.

(Continued from p. 152.)

II. As a second argument against the existence of hydrogen peroxide in the atmosphere, Iloswa advances the fact that it cannot be demonstrated by the reagents, which he considers as exclusively characteristic. In strictness he accepts only one characteristic and certain reagent—a solution of titanic acid in concentrated sulphuric acid. He accepts the reaction with chromic acid ether only if the absence of ozone has been demonstrated, and entertains even some doubts as to its trustworthiness.

On my part I can confirm that it is not practicable to demonstrate by means of these two reagents with certainty the existence of hydrogen peroxide in atmospheric precipitations (natural or artificial), and from the simple reason that they are not sufficiently sensitive.

Iloswa found that with titanic acid a proportion of hydrogen peroxide less than 1·90,000 cannot be detected, and with chromic ether only 1·8500.†

In the district of Moscow in the years 1874 and 1875 I have never found more than 1·2 m.grms. hydrogen peroxide per litre of atmospheric water, *i.e.*, scarcely more than one-millionth, and this maximum quantity only in two cases out of more than five hundred. Although in Hungary, which lies more to the south, rather more hydrogen peroxide may in rare cases occur in the rain, its quantity will certainly not reach the limit at which, according to Iloswa, titanic acid is available for the detection of hydrogen peroxide.

III. Iloswa further advances as an argument against the presence of hydrogen peroxide and of ozone that we do not know—at least not with certainty—of any process by which they may be formed in nature. As regards ozone he found that it is not produced by the evaporation of the water of an artificial reagent. He does not indicate, however, how the experiment was conducted and by what means the non-formation of ozone was demonstrated. He excludes *a priori* the formation of ozone by the slow combustion which takes place in nature, since otherwise its chief quantity would be found near the surface of the earth, which, however, is not the case.

Here Iloswa, remarkably enough, relies on the authority of Hartley and Scoutetten, who are amongst the most zealous advocates of atmospheric ozone. Moreover, arguments *a priori* are not accepted in the exact sciences.

That on the electric discharge of lightning there is a production, not of ozone, but of the oxides of nitrogen, I do not dispute. Iloswa admits the formation of ozone by the silent discharge, but raises the question concerning the constant presence of ozone in the air "whether this silent discharge is constant," to which question he supplies no answer.

Even if we were willing to admit that we know of no sources of ozone in nature, we cannot admit this circumstance as an argument against its presence in the air. We are ignorant of the origin of thousands of things occurring in nature; but no one on that account questions their existence as soon as it is proved by certain methods. The question of the existence of atmospheric ozone and of hydrogen peroxide is not decided by considerations about their possible origin, but by exact methods for their detection in the air.

Iloswa holds the reactions hitherto used for the detection of atmospheric ozone as invalid, since they are also occasioned by nitrous acid. He would not err if this acid were to occur in the air in a free state, which, however, is not the case (see above).

(To be continued.)

* *Berichte der Deutschen Chemischen Gesellschaft*, xxvi., p. 3011.

† By a correct use of this reagent (TiO_3) I have succeeded in recognising a proportion about ten times smaller, but even then its sensitiveness does not suffice for detecting the presence of hydrogen peroxide in the atmosphere and in its downfall.

A PLEA FOR GREATER COMPLETENESS IN CHEMICAL ROCK ANALYSIS.

By W. F. HILLEBRAND.

The valuelessness to the mineralogist and geologist of many of the analyses of mineral substances made in earlier times is a fact too well known to need substantiation. Defective methods of analysis, the difficulty of procuring pure reagents, and want of time for exhaustive examination have been largely responsible for this condition; but lack of appreciation of the fact, now so well established, that substances present in small amount may have an important bearing on the discussion of results, has no doubt contributed in no small measure to it.

Whatever the causes, the result has been the necessity for a vast amount of repetition in analytical work, and it behoves the present generation of chemists to heed well the warning and to work with a two-fold purpose in view, that of lightening the labours of those who come after us by enabling them to use our work with less supplementary examination, and of thereby enhancing our own reputations by meriting encomiums on work that has stood the test of time.

This monition applies to the lithologist as well as to the chemist, and the former should seek to make or have his analyses made as complete as possible, and not, as is so often the case, be content with determinations of silica, alumina, the oxides of iron, lime, magnesia, the alkalis, and water; even going so far sometimes as to ask the chemist to omit tests for other constituents that may be present in small quantity for the sake of getting a greater number of more or less incomplete analyses accomplished. The latter, it is true, may serve the immediate purpose for which they were intended, but their incompleteness may, on the other hand, not only conceal points fruitful of suggestion to the attentive mind, but, what is of still greater importance, they may be actually misleading. Enough instances of totally inaccurate conclusions to be drawn from them have fallen under my own observation to fully justify this plea in favour of greater completeness in rock and mineral analyses made for purely scientific purposes.

This is shown by the difference between the following

analyses. The specimens were taken and analysed at widely separated times and by different persons, it is true, but they were unquestionably from the same rock mass in which, however much the relative proportions of the different mineral constituents might vary within certain limits, there can be no reason to doubt the general distribution of all the elements shown by the second analysis.

	Earlier analysis.	Later analysis.
SiO_2	54·42	53·70
TiO_2	—	1·92
Al_2O_3	13·37	11·16
Cr_2O_3	—	0·04
Fe_2O_3	0·61*	3·10*
FeO	3·52*	1·21*
MnO	—	0·04
CaO	4·38	3·46
SrO	—	0·19
BaO	—	0·62
MgO	6·37	6·44
K_2O	10·73	11·16
Na_2O	1·60	1·67
Li_2O	trace	trace
H_2O below 110° C ..	—	0·80
H_2O above 110° C ..	2·76†	2·61
CO_2	1·82	—
P_2O_5	—	1·75
SO_3	—	0·06
F	—	0·44
Cl	—	0·03
	99·58	100·40
Less O for Fl ..		0·19
		100·21

Another instance of a similar kind is given below. Here again certain differences are explainable by natural variations in the proportions of the constituent minerals, but it can hardly be doubted that TiO_2, BaO, SrO, P_2O_5, and SO_3 were present in both specimens in approximately the same amounts. In the earlier analysis in this case determinations of some supposed unimportant constituents were purposely omitted or only made qualitatively, with results which cannot be otherwise than fatal to a full comprehension of the mineralogical nature of the rock.

	Earlier analysis.	Later analysis.
SiO_2	44·31	44·65
TiO_2	not est.	0·95
Al_2O_3	17·20	13·87
Fe_2O_3	4·64	6·06
FeO	3·73	2·94
MnO	0·10	0·17
CaO	10·40	9·57
SrO	—	0·37‡
BaO	—	0·76
MgO	6·57	5·15
K_2O	3·64	4·49
Na_2O	4·45	5·67
Li_2O	—	trace
H_2O below 110° C ..	0·77	0·95
H_2O above 110° C ..	—	2·10
H_2O by ignition ..	3·30	—
CO_2	—	0·11
P_2O_5	—	1·50
Cl	—	trace
SO_3	—	0·61
	99·11	99·92

* From the fact that repeated determinations of the iron oxides in this and related rocks from the same region show always a great preponderance of ferric oxide, it is not improbable that the figures given for the two oxides in the first analysis were accidentally transposed.

† In the published analysis it does not appear whether this is total water or, as seems probable, only that remaining above 100° C.

‡ Not entirely free from CaO.

While strongly upholding the necessity for more thorough work, necessarily somewhat at the expense of quantity, it is far from my intention to demand that an amount of time altogether disproportionate to the immediate objects to be sought should be expended on every analysis. But I do maintain that in general the constituents which are likely to be present in sufficient amount to admit of determination in the weight of sample usually taken for analysis—say 1 grm. for SiO_2, Al_2O_3, &c., to 2 grms. for certain other constituents—should be sought for, qualitatively at least, in the ordinary course of quantitative work, and their presence or absence noted among the results. If present in little more than traces that knowledge alone may suffice, for it is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0·02 or 0·06 per cent. In the tabulation of analyses a special note should be made in case of intentional or accidental neglect to look for substances which it is known are likely to be present. Failure to do this may subject the analyst to unfavourable criticism when at some future time his work is reviewed and the omissions are discovered by new analyses.

Finally, whenever possible, a thorough microscopical examination of the rock in thin section should precede the chemical analysis. This may be of the greatest aid to the chemist in indicating the presence of unusual constituents or of more than customary amounts of certain constituents, whereby possibly necessary modifications in the analytical procedure may be employed without waste of time or labour.—*Journal of the American Chemical Society*, xvi., No. 2.

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

Second Paper: the Analysis of Baric Chloride.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 151.)

In the experiments (First Series) the baric chloride was ignited in the air, and the small amount of chlorine lost was allowed for as usual. The calculated and carefully weighed amount of pure silver was dissolved in nearly three times its weight of the purest nitric acid in a Bohemian flask provided with bulb tubes for arresting the spray. The bulbs were washed out into the flask, the nitrous fumes were expelled by heating upon the steam bath for a long time, the contents of the flask were diluted and cooled, and the argentic nitrate was added to the baric chloride in a glass-stoppered flask.

In every case the first readings of the end-points are recorded in this Table as being the most trustworthy, although in some cases as much as three weeks were spent upon a single determination in titrating backward and forward. The weights are, as usual, reduced to the vacuum standard.

The objections to this method have been stated already; accuracy with it is a question of judgment and keenness of sight upon the part of the observer, and absolutely constant conditions of temperature, illumination, and agitation on the part of the substance in the flask. Although great pains were taken to have these conditions as constant as possible, it cannot be claimed that they were absolutely so. Moreover, the method is so hopelessly tedious that it was finally abandoned.

In the search for a new method, the following scheme was devised. A slight excess of one or two decigrms. of silver over and above the amount required to precipitate a weighed quantity of baric chloride was weighed out

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*,

RATIO OF SILVER TO BARIC CHLORIDE.

First Series: Stas's Second Method.

No. of Expt.	Corrected weight of Anhydrous Baric Chloride.	Mean amount of Silver required.	Difference between extreme amounts of Ag.	Ratio $2Ag : BaCl_2 = 100 : x$.	Atomic weight of Barium.
	Grms.	Grms.	Grm.		
30.	5·9717	6·1872	0·0032	96·517	137·431
31.	5·4597	5·6580	0·0140	96·495	137·383
32.	3·4728	3·5988	0·0050	96·499	137·389
33.	9·0726	9·4010	0·0160	96·507	137·408
34.	0·6950	0·7199	0·0029	96·541	137·482
				96·511	137·419

Second Series: First New Method,

No. of Expt.	Corrected* weight of Baric Chloride.	Silver weighed out.	Weight of Silver found in filtrate.†	Weight of Silver corresponding to $BaCl_2$.	Ratio $2Ag : BaCl_2 = 100 : x$.	Atomic weight of Barium.
	Grms.	Grms.	Grm.	Grms.		
35.	6·36974	6·72090	0·12097	6·59993	96·512	137·419
36.	5·36010	5·73383	0·18154	5·55229	96·539	137·476
37.	3·92244	4·08060	0·01680	4·06380	96·522	137·440
				Average	96·524	137·445

* For the corrections see *ante*, p. 137. These three analyses are portions of Expts. 20, 26, and 27.

† This weight, computed from the argentic bromide, has been corrected for a very slight excess of hydrochloric acid. The correction, which was of course added, amounted to 0·00026 grm. in the first case, 0·00007 in the second, and 0·00009 in the third. Compare data on p. 137.

Third Series: Second New Method.

No. of Expt.	Corrected* weight of Baric Chloride.	Weight of Silver taken.	Silver found in one half of filtrate, plus correction of 0·0001 grm.	Silver corresponding to Chlorine found in the other half of filtrate.	Corrected Silver required by Baric Chloride.	Ratio $2Ag : BaCl_2 = 100 : x$.	Atomic weight of Barium.
	Grms.	Grms.	Grm.	Grm.	Grms.		
38.	4·2815	4·43558	0·00080	0·00076	4·4355	96·528	137·453
39.	2·6488	2·74417	0·00063	0·00054	2·7440	96·531	137·459
40.	5·9712	6·18547	0·00065	0·00118	6·1865	96·520	137·436
41.	3·2841	3·40245	0·00060	0·00052	3·4023	96·526	137·449
					Average	96·526	137·449

* The last two of these determinations formed a continuation of Expts. 28 and 29 already given, and the calculation of the amount of anhydrous baric chloride need not be repeated. The actual weight of ignited baric chloride taken in Expt. 39 was 2·64851 grms. (in vacuum); but this was found to require a correction due to loss of chlorine amounting to 0·00025 grm. The corrected weight is given in the Table. Since the salt used in Expt. 38 was ignited in hydrochloric acid gas, no correction was necessary. In Expt. 38 the weight of silver given in the third column is 0·00020 grm. less than the amount actually weighed, because 0·20 c.c. of standard hydrochloric acid was added to determine the neutrality of the baric chloride before the precipitation.

with the greatest care. This was dissolved and added to the baric chloride as before. The mother liquor, containing argentic nitrate, baric nitrate, and nitric acid, *but no trace of chlorine*, was filtered off with the greatest care through asbestos, and the precipitate was thoroughly shaken and washed with pure water. The wash waters were collected separately and evaporated on the steam bath in a suitably covered dish to small bulk. The trace of argentic chloride thus precipitated from them was filtered off and washed upon a very small filter, and the few m.grms. of argentic nitrate in the filtrate were added to the original mother liquor. From this mixture of liquids all the silver was precipitated and weighed as argentic bromide.* The excess of silver originally weighed out is thus very simply calculated from the weight of the argentic bromide without involving a personal equation of any sort. Three analyses were made according to this method.†

* For the preparation of the hydrobromic acid used, see the *Proceedings of the American Academy*, xxviii., 17. The precipitate was assumed to contain 57·445 per cent of silver.

† After the present paper had gone to press, notice was received from Professor Mallet that Stas had suggested to him, in a letter dated January 27, 1887, a method very similar to the one just described.—J. W. Mallet, "Stas Memorial Lecture," p. 63. (Nov. 12, 1893).

A second new method of accomplishing the desired object consisted in the actual determination of the silver and chlorine left in a solution obtained by mixing amounts of baric chloride and argentic nitrate supposed to be equivalent.

The solution and first five wash waters filtered off from such a carefully prepared mixture, which had been shaken occasionally for about a week, were thoroughly mixed and divided exactly in half. One half was evaporated with hydrobromic acid, and the other with argentic nitrate, and the small amounts of argentic bromide and chloride were determined by reduction and the use of Volhard's method.

Subsequently it appeared that there was a slight error in the method, due to the difficulty of determining accurately such small quantities of substance. By the evaporation of solutions known to contain nothing but pure argentic chloride, it was found that the amount of silver obtained was always a little less than enough to correspond to the chlorine. Several experiments showed that the error from this cause amounted to very nearly one-tenth of a m.grm., hence this amount is added to the amount of silver found in the half of the filtrates which was evaporated with hydrobromic acid.

(To be continued).

CHEMISTS HONOURED IN PARIS.

In previous communications to the Chemical News I have directed attention to gross inaccuracies, and to the want of a liberal spirit on the part of French historians of chemistry, especially in neglecting to give credit to the labours of chemists not born on French soil. It now gives me pleasure to point out a noteworthy instance of liberality, and a gratifying recognition of the world of science in a quarter that I have not seen noted. The municipal authorities of Paris, in naming streets, avenues, and public squares, have perpetuated the names of men of letters, military heroes, statesmen, artists, and musical composers, and have specially honoured eminent men of science, including astronomers, physicists, chemists, naturalists, and philosophers. In selecting these, the authorities have not confined their choice to men of their own nation. In some instances the streets thus designated are appropriately placed near Institutions of learning with which the *savants'* names were associated; in others, names of *savants* engaged in common pursuits are grouped within small areas.

The Jardin des Plantes is bounded by streets named respectively Cuvier, Buffon, and Geoffroy St. Hilaire; while in the immediate vicinity are the streets Lacépède and the Place Jussieu. Elsewhere in Paris the following names occur:—Lamarck, Linnæus, de Saussure, and Humboldt.

Near the École de Médecine, runs the street Dupuytren, and in the same quarter the eminent physician Velpeau is honoured. Near the Hospital La Salpêtrière two English physicians lend their names to streets, Harvey and Jenner. In the Neighbourhood of the Arc de Triomphe occur the names of the astronomers Copernicus, Galileo, Kepler, Euler, and Newton; elsewhere we find the streets Huyghens, Laplace, and Herschell.

Mathematicians and physicists have not been forgotten, as shown by the occurrence of the following street names:—Biot, Pascal, Lalande, Lahire, D'Alembert, Dulong, Arago, Monge, Legendre, Ampère, Fresnel, Becquerel, Galvani, Volta, Franklin, and Faraday. Ampère, Galvani, and Faraday are near each other.

Philosophy is represented by Descartes, Auguste Comte, and Bacon; engineering by Vauban, Watt, Stephenson, and Fulton; useful inventions by Bernard Palissy and Guttenberg; exploration by Christopher Columbus and Magellan.

Chemists have received, however, a larger share of the honours than any other single class, not even excepting men of letters. Thus we find streets named after the French chemists Bayen, Berthollet, Cadit, Chaptal, Darcet, Daguerre, Gay-Lussac, Lavoisier, Langier, Orfila, Parmentier, Payen, Raspail, Réaumur, Rouelle, Thénard, and Vauquelin; the Swede Berzelius; and the Englishmen Davy, Faraday, Priestley, Cavendish, and Watt.

Even alchemy is represented; near the beautiful Tour St. Jacques de la Boucherie, two streets cross each other at right-angles, named respectively Nicolas Flamel and Pernelle; the history of the alchemist Flamel and his faithful wife is known to all readers of the Chemical News.

This note is intended to apply to men of science, but before closing it may be of interest to record the names of eminent men in other professions who are commemorated in Paris streets. Musical composers—Auber, Beethoven, Cherubini, Meyerbeer, Mozart, and Rossini. Artists—Ribera, Rembrandt, Ruysdael, Murillo, Raphael, Rubens, Leonardo da Vinci, Teniers, Van Dyck, and Velasquez. Men of letters—Balzac, Corneille, Alex. Dumas, La Fontaine, Lamartine, Mirabeau, Molière, Racine, Rabelais, J. J. Rousseau, Voltaire, Goethe, and Lord Byron.

Americans are represented by Franklin, Washington, and Lincoln.

Finally, these lists do not profess to be complete; probably a larger acquaintance with biographical dictionaries would increase this honourable record.—H. C. B.

Paris, March, 1894.

NOTICES OF BOOKS.

A Standard Dictionary of the English Language. New York, Toronto, and London: Funk and Wagnall's Company. Vol. I. from A to L.

The time has undoubtedly arrived when the once derided "American language" has become a power in the land. Messrs. Funk and Wagnall's Co. have, after four years of immense labour and great cost, produced a dictionary which commands our highest admiration. Nearly two hundred editors have been engaged upon the various departments, every one being an American or English scholar of the foremost rank. One of the most distinguishing features of this work is the boldness with which the editors have adopted what has been called "scientific spelling." To use their own words, "In its effort to help to simplify the spelling of words, this dictionary is conservative, and yet agressively positive, along the lines of reform agreed upon almost unanimously by all the leading philologists of America and England."

About 3500 words are given a place in this dictionary to which the principles of the Spelling Reform have been applied.

In chemical nomenclature we see no objections to leaving out the final *e* in *chlorin*, *bromin*, *oxid*, &c.; but when we read *fosforus*, *fosfats*, *sulfur*, and such like, we must confess to feeling a kind of "mental wrench." The beauty of the English spelling (though often called barbarous) lies in the fact that we can through its means trace the origin or derivation of the word. If, however, it has to give way to "fonetic" spelling, then farewell to philology. Democracy is making rapid strides in these days, but we think most Englishmen have in their hearts a fondness for old institutions and traditions.

In comparison with other dictionaries we find the one now under notice includes many thousands of new words. It is also illustrated with many woodcuts and excellent lithographic plates; the one illustrating "gems" we have rarely, if ever, seen surpassed. The print, though small, is very distinct, and everywhere we find evidence of the extreme care which has been bestowed on its compilation. Without wishing to be hypercritical we may mention one little slip which has caught our eye. On turning to the word "*enough*" we are referred to "*enuf*," but on looking for the latter we rejoice to find it has been omitted. Evidently the editor's courage failed him when he saw the awful appearance of the combination of letters ENUF. No matter how carefully proofs are corrected, mistakes will occur.

A very convenient novelty deserving of notice is the method adopted for enabling one to instantly turn to any desired letter. The edges of the leaves are cut with indentations, forming the section of a cone, the basic being the first page of each letter. The letter itself is printed opposite the indentation on the margin of every page, so that we can see at a glance where to put the finger to any letter we wish to find.

Calming the Waves. ("Die Lehre von der Wellenberuhigung"). By Dr. M. M. Richter. Berlin: R. Oppenheim (Gustav Schmidt). 1894.

There is a well-known dictum that "there is nothing new under the sun." This old saying, unlike so many others of its class, has the merit of containing at least a modicum of truth. It applies with great force to the sub-

ject of the pamphlet now before us, on "The Study of Wave Calming." The knowledge of the action of oil in quieting waves is of great antiquity. It was evidently well known before the dawn of the Christian Era, and who can say for how long before that? But, in spite of this fact, we are constantly hearing that it has, so to speak, been re-discovered. Dr. Richter, however, does not put forward any claim of this sort, but he urges, with apparent good reason, the more general application of the use of oil in rough seas by all classes of sea-going vessels. As a result of his investigations, he finds that a so-called "bad oil" is far more suitable for this purpose than a good refined oil, on account of its more rapid spreading over the surface of the waves, due to its partial loss of viscosity, and he gives as his opinion that the safety of a ship (when in danger from rough weather) will depend in the first place on the rapidity with which she can be surrounded with a protective oil belt.

We believe that most ocean-going steamers are now furnished with this means of protection, but there still remains much to be done before its use becomes universal.

The Quantitative Determination of Arsenic in Wall-papers by the Berzelius-Marsh Process. On the Formation of Volatile Compounds of Arsenic from Arsenical Wall-papers. On Chronic Arsenical Poisoning from Wall-papers and Fabrics. By Charles R. Sanger. Reprinted from the *Proceedings of the American Academy of Arts and Sciences*, vols. xxvi. and xxix.

A large portion of these papers is simply historical, the author going back as far as the year 1815 in reviewing a number of cases of arsenical poisoning.

In the first paper he describes the work done by Marsh, Berzelius, and others on the quantitative estimation of small quantities of arsenic by direct weighing, and points out that the first practical application of their methods was made by Gautier in 1876.

He then gives in detail the methods of comparison of mirrors as he has used it in the analysis of wall-papers, making reference to the analytical and experimental work which follows. This also is all given in full, and finally the results obtained by the Berzelius-Marsh and other processes are compared.

Before the process herein described was worked out, it was thought that merely an approximation of the amount of arsenic would be given, but it has been found that with care it can be made to give results worthy of comparison with other quantitative methods. The process is expected to be of great value in toxicology, not only as a rapid means of determining the quantity of arsenic present, and as a check on other methods, but also as the only means of accurately determining the amount when arsenic is present in minute quantity. The extreme sensitiveness of the method can be seen from the fact that as little as 0·0007 m.grm. of arsenic has been detected with certainty.

The two following papers deal with the mechanical means by which the poison is actually introduced into the system, and the methods of getting rid of it again. Experiments are described which were intended to repeat the work of Fleck and Hamberg, and which were based on the assumption that the volatile compound, if formed, would be arseniuretted hydrogen, but on account of their negative results they are not given in much detail, for the conclusions arrived at were shown by a second series of experiments to be erroneous.

This second series of experiments, carried out as closely as possible after the method described by Gosio, whose work on this subject has received but little attention, proved beyond a doubt that there was a volatile compound formed by the decomposition of arsenical matter by the action of mould. Artificial moulds were cultivated, four of which had a very strong action, but it is worthy of note that the most intense action is possessed by the mould discovered on decaying paper, and it must not be forgotten that a small amount of arsenic in a wall-paper may be quite as good a source of the volatile compound as a very large amount. The author has not made any investigation into the nature of the compound, as he considers that such work would be trespassing on Gosio's field, but he thinks the chances are that no arseniuretted hydrogen is formed at all, but that we have to deal solely with an organic compound of arsenic.

The method of diagnosing in cases of suspected arsenical poisoning is fully given, and great stress is laid on the necessity of examining the urine for arsenic, this being one of the most certain indications of the presence of the poison in the body.

CORRESPONDENCE.

THE ARTIFICIAL FORMATION OF THE DIAMOND.

To the Editor of the Chemical News.

Sir,—With your kind permission I wish to make a few observations on an interesting letter in *Nature* of March 22nd from Prof. Joly, in which he concludes from an examination of the curve representing the expansion of diamond by heat that "the diamond is a form of carbon which has been subjected to high pressure when crystallising," and in which he remarks that these theoretical considerations gave rise to experiments which he only laid aside finally upon hearing of M. Moissan's success. He also says "M. Moissan has shown that the *added condition* of high pressure has rendered a method previously unsuccessful *now for the first time successful*." The italics are mine.

Prof. Joly here makes a claim for M. Moissan, which I must say in justice to that gentleman he has never made for himself. If Prof. Joly will kindly turn to my paper on the "Artificial Formation of the Diamond" (*Proc. Roy. Soc.*, No. 204, 1880) he will find that pressure is *not* an "added condition," and that M. Moissan has *not* "rendered a method hitherto unsuccessful for the first time successful."

Further, he will find that his theoretical deductions were practically demonstrated by me fourteen years ago, and I then described experiments showing that carbon set free by metals under great pressure was denser and harder the higher the pressure, and my experiments culminated in the preparation of minute quantities of carbon identical in hardness, density, and action on polarised light with natural diamond.

M. Moissan has done no more, but he has devised a process of great ingenuity, which does not entail the danger and expense of mine, and which can be repeated with much greater chance of success.

If Prof. Joly will turn to my paper he will find that, like Moissan, I obtained my diamond in conjunction with a fused mass containing iron, and fused under extreme pressure. Again, in the *Proc. Roy. Soc.* for June, 1888 (also Chemical News, 1888), he will find that the Hon. C. A. Parsons there describes experiments by which he produced true diamond (thoroughly corroborated since the publication of his paper), and he proved conclusively that pressure is absolutely essential; and as his method is one which lends itself to the treatment of carbon in quantity at the necessary temperature and at any pressure, it is of much greater practical importance than Moissan's method.

I have the highest admiration of Moissan's work, not only with his electric furnace, but in the several fields in which he has distinguished himself; and as he has courteously admitted that I was the first to define the conditions and actually prepare artificial diamond, I feel constrained to point out that both Parsons and I had fully enunciated the conditions which Prof. Joly attributes to Moissan.

I quite agree with Prof. Joly's concluding paragraph, and my researches led me about a year ago to the construction of an apparatus capable of producing pressures up to forty tons on the square inch, in which I have good hopes of being able to melt carbon in quantity, and produce diamond by fusion instead of solution.

Carbon at ordinary pressures passes directly from the solid to the gaseous state, and only under enormous pressure can it be made to pass through the liquid state.

It would be premature for me to say more at present, but I hope you will kindly allow me to put these facts on record, as they seem to have been forgotten even by those who are working in the field.—I am, &c.,

J. B. Hannay.

Cove Castle, Loch Long, N.B.,
March 26, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 12, March 19, 1894.

New Apparatus, named the Monochromatoscope.—Maurice de Thierry.—The construction of this apparatus cannot be shown without the two accompanying figures. With it the author is undertaking the interesting study of the latent colour of substances, formerly indicated by Govi, and applies it to the optical analysis of metallic and organic powders, as well as to the detection of the falsifications of certain alimentary and pharmaceutical substances. Such bodies as mercuric iodide and vermilion, which by sun-light have colours almost identical, differ absolutely in a given ray, which permits us to see no longer the apparent colours of these substances, but their true colours.

General Law of the Solubility of Normal Substances.—H. Le Chatelier.—The author's formula leads to the conclusion that the normal curve of the solubility of a body will be the same in all solvents; but in reality the latent heat of the solution is not constant, and varies a little with the nature of the solvent. The general form of this curve is the following:—It is comprised between two parallel asymptotes: the axis of the temperatures towards null temperatures, and the ordinate—

$$s = \frac{L}{t_0}$$

towards infinite temperatures.

Molecular Weight of Ferric Chloride.—P. Th. Müller.—In boiling alcohol and ether, the molecule of ferric chloride corresponds to the formula $FeCl_3$. The movement of this substance is comparable to that of acetic acid, the vapour of which at 130° contains a great number of double molecules, and which, nevertheless, at 0° in water contains a simple molecule.

Composition and Formation Heat of Hydrated Nitrous Oxide.—M. Villard.—The exact formula of this compound is $N_2O,6H_2O$.

Thallium Hypophosphates.—A. Joly.—The author has obtained and examined the dithallous hypophosphate, $P_2O_6H_2Tl_2$, and the tetrathallous salt, $P_2O_6Tl_4$. The latter salt on exposure to direct solar light turns to an indigo blue.

The Influence of the Manner of Distribution of Manures on their Utilisation by Plants.—A. Prunet.—The author distinguishes *travelling manures, e.g.*, nitrate of soda, always dissolved and infinitely diffusible, and others, such as the phosphatic and potassic manures which are immovable. The latter, even if supplied to the soil in a soluble form, quickly enter into insoluble combinations, the utilisation of which depends on their meeting with the roots of plants.

β-Dibromopropionic Acid.—R. Thomas-Mamert.—This compound is obtained by the action of fuming hydrobromic acid at 100° in sealed tubes on tribromopropanoic acid, melting at 115°. It melts at 71°. It crystallises in the orthorhombic system.

Journal fur Praktische Chemie.
Vol. xlix., Parts 2 and 3, 1894.

Researches from the Chemical Laboratory of Prof. Alexander Saytzeff at Kasan.—These researches comprise a paper on allylmethylethylcarbinol and the heptylglycerin thence obtained, by Nic. Saytzeff; a memoir on allylmethylhexylcarbinol and the hendecatylglycerin thence obtained, by Al. Bojanus; a memoir on methylethylpropylethylenglycol, by Joh. Panfiloff; and one on isoerucic acid, by P. Alexandroff and Nic. Saytzeff.

Isomeric Octonaphthenic Acids.—B. Markownikoff.—These compounds are otherwise known as cyclohexanmethylcarbonic acids. We find a description of the orthomethylnaphthenic acid, its salts, its methyl ether, and its amide; metaoctonaphthenic acid, otherwise named hexahydrometatoluylic acid or cyclohexanmethyl carbonic acid, with its salts; paramethylnaphthenic acid with its derivatives.

The Action of Sodiummalonicethylester on Cyanous Chloride.—Wilh. Kolb.—This paper does not admit of useful abstraction.

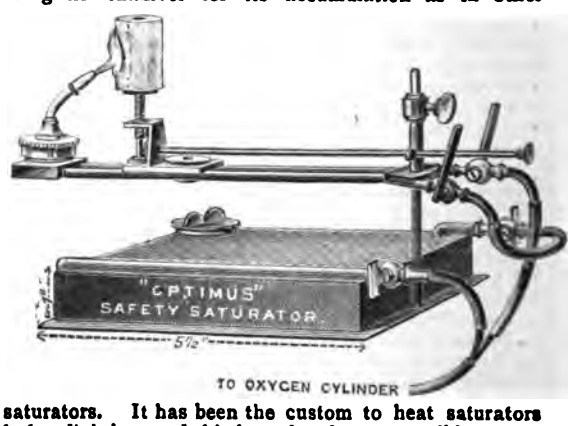
Calorimetric Researches.—F. Stohmann.—A discussion of the thermic value of aliphatic acids.

On Naphtholic Ether Derivatives.—P. Heermann.—A paper on the sulphonation of α- and β-naphthol-ethyl ethers.

Stereo-chemistry.—Dr. Seelig.—The author concludes with the question, how is chemistry to be benefitted by stereo-chemical views?

MISCELLANEOUS.

Messrs. Perken, Son, and Rayment have just introduced their "Optimus Safety Saturator" for optical lantern illumination. They assert that in this apparatus the maximum degree of safety has been attained, as no accumulation of mixed vapour can exist therein, there being no chamber for its accumulation as in other



saturators. It has been the custom to heat saturators before lighting, and this has often been a possible source of danger; the inventors of this form of instrument do not agree with heating, and call special attention to the fact that the "Optimus Safety Saturator" is designed for the express purpose of avoiding any heating whatever.

Insanity.—According to the *Medical Presss*, the latest returns show that in this country "rather more than thirty persons out of every ten thousand are of unsound mind." This estimate, drily remarks our contemporary, "does not include the anti-vivisectionists, the anti-vaccinationists, and some others," meaning, we presume, the faddists in general.

MEETINGS FOR THE WEEK.

MONDAY, 9th.—Society of Arts, 8. (Cantor Lectures). "Photometry," by Capt. W. de W. Abney, C.B., F.R.S.
TUESDAY, 10th.—Royal Institution, 3. "Electric Illumination," by Prof. J. A. Fleming.
—— Medical and Chirurgical, 8.30.
—— Institute of Civil Engineers, 8.
—— Photographic, 8.
—— Society of Arts, 8. "The Evolution of Decorative Art," by Henry Balfour, M.A.
WEDNESDAY, 11th.—Society of Arts, 8. "London Coal Gas and its Enrichment," by Prof. Vivian Lewes.
—— Geological, 8.
—— Pharmaceutical, 8.
THURSDAY, 12th.—Royal Institution, 3. "The Etching Revival," by F. Seymour Haden.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
—— Chemical, 8. "Action of Metals on Strong Acids," by G. J. Burch, M.A., and J. W. Dodgson. "Action of Light on Oxalic Acid," by Dr. A. Richardson. "English Jute Fibre. II." by A. Pears, jun. "Natural Oxycelluloses," by C. Smith.
FRIDAY, 13th.—Royal Institution, 9. "Some Properties of the Electric Discharge through Gases," by Prof. J. J. Thomson, F.R.S.
—— Astronomical, 8.
—— Physical, 5. Discussion of Prof. Henrici's paper on "Calculating Machines." "On the Minimum Temperature of Visibility," by P. L. Gray. "On the Mechanism of Electrical Conduction," by Dr. C. V. Burton.
SATURDAY, 14th.—Royal Institution, 3. "Life among the Afghans," by J. A. Gray.

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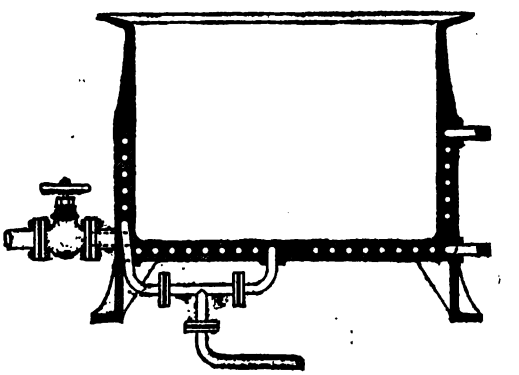

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says;—

P. 316. "An improved vessel for boiling oil, and suitable for many other kindred purposes, has been recently described by T. Frederking (CHEMICAL NEWS, London). A coil of stout piping is arranged in a casting mould, so that the molten metal forming the pan is cast round the coil, much as is done in the case of the water-tuyeres of a blast furnace. Steam at any pressure [or any other heating medium] being passed through the coil, the pan is heated up proportionately without any danger, the pressure bearing solely on the piping and not on the metal pan itself, whilst the well conducting metal walls allow the heat to pass readily. Temperatures up to 350° and 400° C. can be thus obtained."

Messrs. KALLE & Co., Manufacturers of Aniline Colours, Biebrich (Rhine), in their letter of November 22nd, 1893, say:—

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Messrs. C. and G. MÜLLER, Rixdorf, near Berlin, S.O., in their letter of December 22nd, 1893, say:—

"Concerning the Patent Vessel which you delivered to us, we beg to inform you that it has been in work four months to our entire satisfaction. The security in working with high pressure is especially satisfactory. With your Patent Vessel we are able to put through much larger quantites of tallow in less time than with our previous plant."

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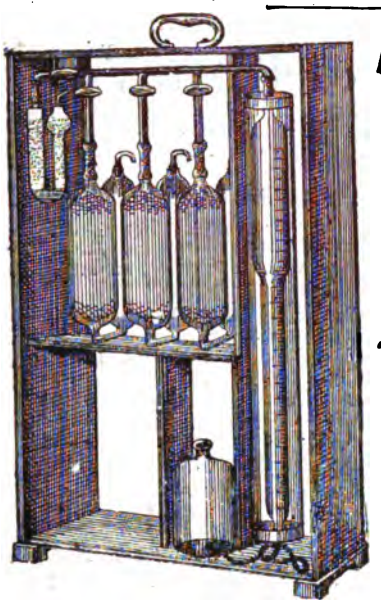

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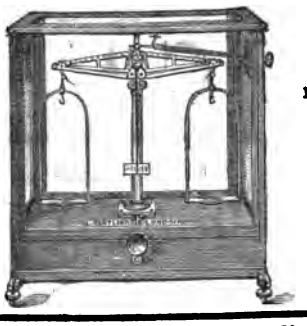

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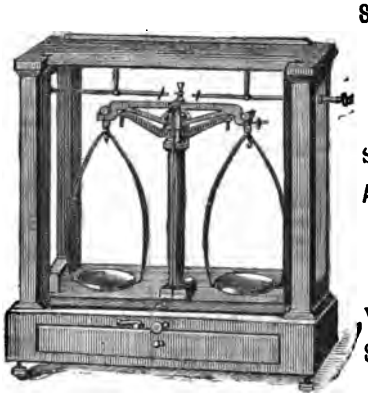

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Vol. LXIX., No. 1794.

THE ESTIMATION OF SILICA.

By ALEXANDER CAMERON.

The estimation of silica has been the subject of a number of investigations. Within recent years we have had laid before us, through the medium of various periodicals, articles on this subject based on experiments performed on substances, such as clays, in which the total amount of silica was doubtful; and there being so many impurities present, such as alumina, iron, and lime, whose influence is not exactly known, the various methods recommended for the estimation of silica have not been properly compared with each other. The proper method of comparing these methods is to obtain a sample of pure silica and experiment on it; but as absolutely pure silica is difficult to obtain, I had to employ a silica containing about 98·5 per cent of pure SiO_2, the remaining 1·5 per cent being made up of about 0·1 per cent Fe_2O_3, 0·5 per cent Al_2O_3, 0·7 per cent CaO, and 0·2 per cent MgO.

In each experiment 2 grms. of the silica (freshly ignited) were used, unless otherwise stated. This silica was fused over the blowpipe for about fifteen minutes with about 9 grms. of fusion mixture, the fusion when cold being decomposed with hydrochloric acid, and evaporated to dryness in a porcelain basin, the heat being continued for some time after all acid fumes were driven off.

When the dehydration was effected over the water-bath at 100° C., I found that the main silica precipitate was less than if the dehydration had been effected over the blue flame of an Argand burner, and consequently that more silica remained in solution after filtering off the precipitate. Reference may here be made to the Tables. Experiments 1, 2, 3, and 4 illustrate what I have said. These were dehydrated over the water-bath, and the silicas first recovered are all less than in Experiment 5, *et seq.*, which were dehydrated over the blue flame of an Argand burner. As in all other experiments, the silicas here were volatilised with hydrofluoric acid, and the residues obtained deducted, to get true SiO_2.

The filtrates of Nos. 1, 2, and 3 were next evaporated to dryness with sulphuric acid. This treatment of the filtrates is a favourite one, and is said to give better results than if the filtrates were evaporated without any addition being made. It is also stated that about 20 c.c. of sulphuric acid should be added, and evaporated till the acid fumed strongly.

In Experiments 1 and 2, however, I only added a small quantity of sulphuric acid, say about 5 c.c., in evaporating the filtrates to dryness, which was not sufficient to prevent the sulphates produced from crystallising out on evaporation.

In Experiment 3, 20 c.c. of strong sulphuric acid were added to the filtrate from the main silica precipitate, and the evaporation carried out till the sulphuric acid fumed strongly.

On comparing the results of the three experiments it will be seen that a large excess of sulphuric acid is not capable of rendering any more silica insoluble than a small excess.

In these experiments we have to notice the large proportion of silica recovered from the first filtrates, and that four or five evaporations were necessary to recover the silica. The evaporation of filtrates from the main silicas is, at any rate, always imperative, and even the evaporation of the second and third filtrates is necessary until the percentage of silica recovered is reduced to a minimum—say, 0·25 per cent—which might be considered a sufficient indication, as shown by the results in the tables, that practically all the silica had been recovered.

Seeing that these results were given in the case of the evaporation of the filtrates with sulphuric acid, I wished to see what effect would be produced if the evaporation was carried out with hydrochloric acid only. Experiments 4 and 5 represent two experiments carried out in this manner, and two deductions of importance can be drawn from these results.

Firstly, Experiment 4, as compared with Experiments 1, 2, and 3, shows practically the same results, although in the former 20 c.c. of hydrochloric acid was used in the evaporation of the filtrates from the main silica, and in the latter (1, 2, and 3) varying proportions of sulphuric acid were used. We would therefore be justified in concluding that hydrochloric acid gives equally good results as compared with sulphuric acid in rendering the silica in the filtrates insoluble. The advantage of this knowledge cannot be over-estimated, as sulphuric acid is very objectionable where alumina is present, and also iron, both of which are apt to form compounds with sulphuric acid which are soluble with great difficulty in hydrochloric acid, and consequently troublesome to get rid of.

Secondly, Experiments 4 and 5, when compared side by side, show, as stated above, the marked difference the temperature of dehydration makes on the amount of silica recovered. Whereas, in Experiment 4, four evaporations over the water-bath were necessary, in Experiment 5 only two were necessary, as the temperature of the blue argand flame was employed to dehydrate the silica in this case.

The effect of alumina along with the silica was next tried. For this purpose I added 0·2 grm. of pure precipitated alumina, previously ignited and ground finely in an agate mortar, and fused it up with the silica as before. This was equal to an addition of 10 per cent of Al_2O_3. The results may be seen in Nos. 6 and 7.

The filtrates in these cases were treated with sulphuric acid, and evaporated till the acid fumed strongly. As far as the addition of 10 per cent of alumina is concerned, the results show no alteration as far as silica is concerned. Where alumina is present, as I have said, it is objectionable to use sulphuric acid in evaporating the filtrates to dryness, as on taking up with hydrochloric acid and water, previous to filtering, a basic sulphate of alumina is frequently precipitated and is dissolved with great difficulty in hydrochloric acid. If the alumina is thus precipitated, it is necessary to wash free from sulphuric acid before dissolving in hydrochloric acid. To show how little foreign matter, which includes alumina, was left undissolved after this treatment, reference to the residues will show.

I next tried the effect of the presence of varying proportions of iron. In Experiment 8, 8·60 per cent of Fe as ferric chloride was added before starting the fusion. In Experiment 9, where 0·5 grm. of silica was used, 50 per cent of Fe, as ferric chloride, was added after the fusion of the silica had been dissolved in hydrochloric acid, and before taking to dryness. The total SiO_2 in these two experiments corresponds very closely, and this is all the more satisfactory seeing that in Experiment 8 the filtrates were evaporated with sulphuric acid, and in Experiment 9 with hydrochloric acid. And here, again, the superiority of the hydrochloric acid over the sulphuric acid is seen, as the residues obtained from the silicas in Experiment 9 are much smaller than those in Experiment 8, where sulphuric acid was used. In the main silicas the residues are as 0·65 per cent is to 0·05 per cent, *i.e.*, higher where sulphuric acid was used, although the percentage of iron present was only one-sixth of that in Experiment 9.

When sulphuric acid is present along with iron, on evaporation an iron compound is precipitated which is soluble with very great difficulty in the hydrochloric acid added before filtration. Therefore sulphuric acid should not be used in evaporating the filtrate from the main

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SiO_2 in 1st filtrate	3·22	—	3·07	—	2·75	—	2·79	—	1·74	—	1·07	0·10
,, 2nd ,, ...	0·62	—	0·35	—	0·42	—	0·37	0·05	—	—	0·44	—
,, 3rd ,, ...	0·09	0·15	0·24	0·22	0·02	—	0·07	0·12	—	—	0·17	0·15
,, 4th ,, ...	—	—	0·15	0·05	—	—	—	—	—	—	—	—
Total SiO_2, per cent ..	98·23	—	98·54	—	98·21	—	98·35	—	98·58	—	98·47	—

	No. 7.		No. 8.		No. 9.		No. 10.		No. 11.		No. 12.	
		HF Residues. P.c.		HF Residues. P.c.		HF Residues. P.c.		HF Residues. P.c.		HF Residues. P.c.		HF Residues. P.c.
Main SiO_2 precipitate ..	97·39	0·60	95·84	0·65	95·10	0·05	95·47	0·25	96·77	0·30	95·75	0·30
SiO_2 in 1st filtrate	0·87	0·22	1·97	0·83	2·90	0·07	1·65	—	1·22	0·10	1·70	0·10
,, 2nd ,, ...	0·17	0·20	0·32	2·75	0·20	0·05	1·22	—	0·27	0·07	0·98	—
,, 3rd ,, ...	—	—	—	—	—	—	0·05	—	—	—	—	—
,, 4th ,, ...	—	—	—	—	—	—	—	—	—	—	—	—
Total SiO_2, per cent ..	98·43	—	98·13	—	98·20	—	98·39	—	98·26	—	98·43	—

silica in iron ores and such like substances, but hydrochloric acid, as it gives equally good results and is much more satisfactory to work with.

We can also deduce from these experiments that the presence of iron does not affect the estimation of silica.

Another experiment (No. 10) was tried to find what effect the addition of 10 per cent of calcium carbonate would have on the estimation, the filtrates being evaporated with sulphuric acid. The result will be seen to compare closely with the experiments on the pure silica, Nos. 1 to 5.

Nor does the presence of organic matter seem to affect the determination of the silica, as the result of Expt. 11 will show. The organic matter, however, is charred on the addition of sulphuric acid to the filtrates from the main silica, and precipitated, and hinders filtration and washing.

The next point I wished to investigate was whether by repeated evaporation I could increase the amount of silica first recovered. The fusion in this case (Expt. 12) was evaporated three times with 20 c.c. of hydrochloric acid and 20 c.c. of water each time, but the result shows no improvement on the single evaporation method.

City Analyst's Laboratory,
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ON THE CRYSTALLISATION OF GOLD IN HEXAGONAL FORMS.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

While experimenting upon the reduction of gold from a solution of the double chloride of gold and sodium in water, by various metallic sulphides ("On the Formation of Gold Nuggets," *Journ. Roy. Soc. N.S.W.*, 1893, p. 17), I found that in certain cases the gold was deposited on the sulphides in the form of minute prisms and six-rayed stars.

The solution used was the ordinary one employed in toning photographs, *i.e.*, 15 grains of the $AuCl_3,NaCl2H_2O$ to 15 ounces water; freshly fractured fragments of the sulphides were immersed in this and left until a sufficient amount of gold had been reduced and deposited upon them, as stated in the paper referred to; the gold was usually deposited in ochre-coloured, lustreless, mammillated films, but when copper pyrites was used the gold was in some cases also deposited in minute prisms, beautifully sharp and well defined; many of the prisms were grouped in tufts, and in the form of exquisitely arranged six-rayed stars or in groups of three fan-like rays, the rays in both forms meeting at angles of 60° and resembling snow crystals in miniature, but of a most brilliant metallic lustre, and of the colour of the purest gold. In other instances the gold was in the form of six-sided plates.

When a "graphitic casing" from an auriferous vein was used as the reducing agent, the gold was in part deposited in the form of minute very brilliant hexagonal plates.

With zinc blende, in one instance, a few bright apparently crystallised points of gold were intermingled with the dull mammillary gold, also a few well-defined six-rayed stars, and one very distinct St. Andrew's Cross, *i.e.*, a six-rayed star with one transverse pair of rays left out; these may have been broken off or never formed.

Microscopic hexagonal stars of brilliant gold were also deposited on mispickel and on native silver sulphide associated with mammillary gold.

On marcasite a few bright specks were deposited, probably incipient crystals, but no recognisable forms.

In no case were there any traces of gold in forms belonging to the cubical system, although these are so readily obtained by reducing gold with ether, phosphorus in ether, oxalic acid, ferrous sulphate, &c.

The occurrence of gold in prismatic and hexagonal forms has been observed by others; Prof. W. P. Blake describes Crystallised Gold in Prismatic Forms (*Am. Journ. Sci.*, xxviii., 1884). From near Clancy, Clancy Creek, Jefferson County, Montana, were obtained prismatic crystals of gold terminated by an octahedral head or knob, the whole having a comet-like appearance. The total length is about 3 m.m. or ⅛ inch, the prism portion is hexagonal in section. (Figures are given in the paper). They are extremely brittle, and appear to cleave or break at right angles to their length. Hence probably an alloy or amalgam.

Small brilliant hexagonal crystals of gold, terminated at each end by pyramids, were found at Sonora, in Tuolumne County, California, and they resemble the artificial prismatic gold crystals obtained by Prof. Chester (*Am. Journ. Sci.*, July, 1878). It is possible that these crystals are also artificial, although similar crystals obtained at Angel's Camp, in the same district, were said to

* A Paper read before the Royal Society of New South Wales.

have been obtained from a cavity in quartz, but Prof. E. S. Dana, in a paper on the Crystallisation of Gold from White Bull Mine (*Am. Journ. Sci.*, xxxii., p. 132), points out that the rhombohedral and hexagonal pyramid forms are due to planes of the 303 which are elongated in the direction of the octahedral axis.

In another paper on the Crystallisation of Gold (*Am. Journ. Sci.*, August, 1886, p. 138) Prof. E. S. Dana refers to hexagonal depressions in gold crystals and of crystalline ribs meeting at 60° and 120°, which are also quite consistent with the cubical system.

Prof. vom Rath in Groth's *Zeitschrift für Krystallographie und Mineralogie*, 1877, describes some crystals of gold from Transylvania, and amongst them a star-like formation from Felsö-banya, each ray being a twin of the four-faced cube (∞ O 2) round a trigonal axis and extended along the diagonal face of the octahedron. He states that the acicular and capillary forms are usually rhombic in section, and consist of elongated cubes terminated by faces of the tetrakis hexagon (∞ O*n*), the striations of the prisms being due to oscillatory combinations of the cube (∞O∞) and four-faced cube (∞O*n*).

A hexagonal prism of gold closed at both ends by a hexagonal pyramid is said to have been found at New Bendigo; this may have been a pseudomorph after quartz (Selwyn and Ulrich, "Phys. Geog. Geology and Mineralogy of Victoria," Melbourne, 1866).

Prof. Chester described some hexagonal crystals of gold (*Am. Journ. Sci.*, 3rd Series, xvi., p. 32), but as they consisted of an amalgam containing 6 per cent of mercury, they can hardly be cited in support of the apparent hexagonal nature of the crystals obtained on the sulphides by reduction.

Prof. Egleston states that petroleum throws down hexagonal crystals of gold from gold chloride.

The crystals obtained by me up to the present are unfortunately very small and require further investigation; it may also prove to be that the hexagonal plates and stars are incipient cubical forms or even gold containing sufficient foreign matter to affect its crystallisation.

I hope to have an opportunity to lay before the Society the results of some further experiments upon the formation of these hexagonal crystals as soon as they are completed.

THE QUESTION OF THE OCCURRENCE OF HYDROGEN PEROXIDE IN ATMOSPHERIC AIR AND IN ATMOSPHERIC WATERS.*

By EM. SCHÖNE.

(Continued from p. 163.)

I have had here to touch briefly upon the objections of Iloswa to the existence of atmospheric ozone, because he uses its alleged non-existence, among other things, as an argument against a source of hydrogen peroxide recognised by L. Carius. The latter has expressed the opinion that hydrogen peroxide is formed by the action of ozone upon ammonia. "Since I have proved," argues Iloswa, "that there is no ozone in the air, it follows, &c." Quite logical if only the premisses were really established.

Further, as a possible source of peroxide in the air, Iloswa mentions the light of the sun, which "as an assistant energy impels the watery vapours contained in the air to continue their oxidation." If this were the case, according to Iloswa, we should find hydrogen peroxide in the water deposited on the outer sides of a vessel containing a freezing mixture and exposed to the sun, which he has never been able to detect.

Here I do not clearly see the causal connection between the possible presence of the peroxide in the artificial dew and the oxidation of the watery vapours under the influence of solar light. Why may not the peroxide, if it had been detected in the water deposited on the vessel, have had another origin, and, *e.g.*, have been formed during rapid combustion, and have been condensed along with the watery vapours? Whether the vessel was exposed to the sun or not is quite indifferent.

Secondly, the slight proportion of hydrogen peroxide in artificial dew could not be detected with the insufficiently sensitive reagents used by Iloswa.

As it is apparent from my communication on the atmospheric peroxide, I have during the summer months of the years 1874 and 1875 prepared artificial dew (or hoar-frost) far more than one hundred times, and, with very few exceptions, I have detected in all the specimens the presence of peroxide by means of sufficiently sensitive reactions, and have determined it quantitatively by the colorimetric process.

From the actual results which I have obtained in these (and in other) researches, I have certainly inferred that sunlight must play a part in the appearance of hydrogen peroxide in the air; but I have not founded this conclusion upon a single observation, *e.g.*, like Iloswa, exposing the vessel for the formation of artificial dew to the sun. On the contrary, my apparatus stood in the dark. I have formed my conclusion from observations and determinations conducted for weeks without interruption by day and night. From these experiments it appeared with full certainty that for the fluctuations of the quantities of the peroxide occurring in the air in the form of vapour there exists a definite daily period and a yearly period. The quantities increase both in the course of the day and of the year in proportion as the sun rises above the horizon, and decrease as it sinks.

Iloswa does not know more than the two above-mentioned possible manners of the formation of hydrogen peroxide in nature—at least he mentions no others. Although it is not at present my purpose to enlarge upon the possible sources of peroxide in the air, I must briefly mention one to which there occur in literature not few references.

It is known that many organic—especially volatile—substances, such as ether, alcohol, terpenes, various oils, ethereal and others, under the influence of sunlight and in contact with air, take up oxygen, and on treatment with water yield to the latter hydrogen peroxide. My researches in 1874 and 1875 showed that the air in winter is very poor in hydrogen peroxide, and its quantity does not notably increase until the layer of snow has disappeared from the surface of the earth, and vegetation begins to be developed. Further, the yearly maximum of peroxide coincides with the season (July) in which vegetation reaches its height. May we not hence conclude that the various volatile ethereal, aromatic, and other substances which plants exhale under the influence of the solar rays and in contact with watery vapour furnish the air at least with a part of its peroxide?

IV. The fourth argument of Iloswa against the existence of hydrogen peroxide in the atmosphere is the contention that it is indeed formed during the rapid combustion of various gases, liquids, and solids, but under such circumstances that it cannot get into the air, especially when the flames come in contact with the water which it "saturates" with peroxide in the course of two or three minutes. Water condensing from a freely burning flame of hydrogen is said, on the contrary, to contain no hydrogen peroxide. Here Iloswa cites as its authority M. Traube (*Berichte*, xviii., 1890 and 1894), who, however, does not maintain this non-formation in a freely burning flame, but ascribes to water upon which the flame is directed only a cooling action, and thereby an effect favourable to the preservation of a larger proportion of peroxide formed.

The origin of hydrogen peroxide in freely-burning flames, especially in that of hydrogen, has previously been placed beyond all doubt by G. Meissner, H. Struve (*Zeit. Anal. Chemie*), and especially by A. Schüller (*Wied.*

* *Berichte der Deutschen Chemischen Gesellschaft*, xxvi., p. 3011.

Annalen, and A. R. Leeds (CHEM. NEWS, xlix., 292, 1870), and that by means of investigations which are more exact than those by which Iloswa believes that he has disproved the formation of peroxide. My own experiments on this point agree absolutely with the conclusions of the four chemists last mentioned.

The question of the formation of ozone on rapid combustion is here left on one side, especially as Iloswa has essentially withdrawn his original denial on the replies of O. Loew and J. T. Cundall.

(To be continued).

SOLVENTS OF CELLULOSE.

By Dr. T. F. HANOUSEK.

CELLULOSE dissolves, as it is well known, in concentrated sulphuric acid, but with conversion into celluloid. This applies also to cell membranes which consist of almost pure cellulose. The most usual solvent is Schweizer's reagent, *i.e.*, recently prepared cupric ammonia. In order to obtain this compound quickly and conveniently, copper filings are placed in ammonia, and the fine blue liquid is regarded as cupric oxide-ammonia. This view, according to Grimaux, is incorrect, as the product obtained consists of ammoniacal copper nitrite and ammoniacal copper oxide. In any case the action of this reagent upon cellulose membranes is so energetic that pure cellulose fibres like cotton and flax present very characteristic phenomena of solution.

Cross and Bevan have recently indicated a new solvent which is able to dissolve cellulose immediately without alteration. It consists of a solution of zinc chloride in two parts by weight of acetic anhydride.

As the action of the solvents of cellulose is of extreme importance, I undertook some experiments with Cross and Bevan's reagent. The results certainly did not come up to my expectations, but I make them known in order to instigate further research in this direction. The reagent was prepared according to the authors' instructions. It appeared as a thick colourless liquid, and the zinc chloride only dissolves gradually. If it is allowed to act upon cotton hairs they appear at first very transparent, clear, and only slightly swollen. The swelling is not sufficient to obliterate the corkscrew-like curvature of the fibres. No solution like that observed in the case of cupric ammonia is produced. On the other hand, the fine structural relations of the cell-wall, the dissociations of its constituents, are most beautifully revealed. The grate-like double stripes of the membrane comes up very sharply, the primary lamina and the secondary stratum deposited upon the former are distinctly separated from each other. I can therefore pronounce this reagent as an excellent means for showing and dissociating the layers, but not as a solvent.

If the mixture is heated to ebullition, the phenomena of tumefaction are certainly somewhat increased, but there is no solution. The flat, tender, so-called dead cotton-hairs become almost invisible, not in consequence of solution, but because their index of refraction is rendered approximately equal to that of the reagent. Experiments were further made with fibres of linen which had been frequently washed; that is, with cellulose fibres which had loosened by wear and tear and partially destroyed. The result was exactly identical; the tumefaction was certainly greater, the structural peculiarities appeared with the utmost distinctness, the well-known nodes resembled each other almost to the vanishing point, but solution was not effected. Similar facts were observed in fibres isolated from a paper made from a mixture of cotton and linen rags. The tumefaction was strongest in fibres of cellulose paper.

It is certainly possible that the experiments with this reagent might have a different result if the quantitative proportions of the reagent were modified. — *Chemiker Zeitung.*

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

SECOND PAPER: THE ANALYSIS OF BARIC CHLORIDE.

By THEODORE WILLIAM RICHARDS.

(Concluded from p. 165.)

DURING a large part of the considerable time consumed by these analyses, experience with the comparison of opalescence was gradually being acquired. The details of this method have been so fully given by Stas that further mention of them need not be made here. For the final experiments the baric chloride was dissolved in a large amount of water, and decomposed by a very slight excess of argentic nitrate in very dilute solution, the silver having been weighed and dissolved with the greatest care. After the mixture had been shaken occasionally for a number of days it was allowed to settle, and two portions of 25 c.c. each were taken out with a pipette. A little hydrochloric acid produced a more evident opalescence in one of these portions than an equivalent amount of silver did in the other, showing that too much silver had been taken. Known amounts of hydrochloric acid were therefore added very gradually to the main mass of the liquid, until, after agitation and settling, two portions of the clear supernatant liquid treated respectively with argentic nitrate and hydrochloric acid showed like intensity of opalescence. This similarity of opalescence was further confirmed by measuring the heights of parallel unknown columns of the two liquids which had been adjudged equally cloudy. From the average of a great number of readings, one could feel reasonably certain of the result within two or three per cent corresponding to an error of not over one or two tenths of a m.grm. of silver in the volume of solution used.

For example, in the first analysis recorded below it was found in three preliminary trials that about 0·30 c.c. of the standard hydrochloric acid should be added to the remaining mixture in order to reach the desired point. This amount was therefore added, and two portions were again taken out, treated as before, and compared.

Solution to which HCl was added.					Solution to which $AgNO_3$ was added.	
9·5	c.m.	in	height	appeared equal to	10·0	c.m.
10·5	,,	,,	,,	,,	10·0	,,
10·3	,,	,,	,,	,,	10·0	,,
10·1	,,	,,	,,	,,	10·0	,,
9·2	,,	,,	,,	,,	10·0	,,
Av. 9·9	,,	,,	,,	,,	10·0	,,

This average shows that the equality of cloudiness was now within the probable experimental error.

It was borne in mind, however, that a fifth of the original solution had been used up in the preliminary tests. Hence the true amount of hydrochloric acid which should have been added to the original solution must be $\frac{4}{5} \times 0{\cdot}3 = 0{\cdot}375$, or practically 0·4 c.c.

Hence, since this amount of hydrochloric acid is of course a direct measure of the excess of silver originally taken, 0·4 m.grm. should be subtracted from the original weight.

It is needless to say that all possible care was used in these final determinations. The reiteration of the countless details would be wearisome, and hence these details are left to be inferred from what has been already written.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences.*

RATIO OF SILVER TO BARIC CHLORIDE.

Fourth Series: Stas's Third Method.

No. of Expt.	Weight of Crystallised Baric Chloride. Grms.	Weight of Anhydrous Baric Chloride. Grms.	Weight of Silver taken. Grms.	Excess of Silver found. M.grms.	Total weight of Silver. Grms.	Ratio 2Ag : $BaCl_2$ = 100 : x.	Atomic wt. of Barium.
42.	7·63356	6·50022(a)	6·7346	0·4	6·7342	96·525	137·448
43.	12·01793	[10·23365]	10·6067	4·4	10·6023	96·523	137·442
					Average	96·524	137·445

(a) This specimen of baric chloride was dehydrated by ignition in a stream of hydrochloric acid. The specimen whose weight is recorded in brackets below it was not ignited; but the weight of the anhydrous salt was computed by means of the proportion 7·63356 : 6·50022 = 12·01793 : x.

The method is the simplest and easiest of the four; and when one has acquired experience in the comparison of opalescence, it is perhaps also the most accurate.

The Atomic Weight of Barium.

The data based upon the two more satisfactory ratios detailed in this paper have been grouped in seven series of determinations. In the first three series, including ten individual experiments upon the first ratio, the individual results are grouped together according to the condition of the baric chloride used as the starting point. This method of grouping was adopted because the analytical conditions were necessarily quite uniform, and the initial state of the salt was the most important variable. This problem having been solved satisfactorily, the accurate decision of the true end-point in the method of Gay-Lussac remained the most important incidental question to be settled during the determination of the second ratio. Hence, the last four series were grouped according to the method of titration.

From the Ratio of Baric Chloride to Argentic Chloride.

		At. wt. of Barium if O=16·000.
I.	Five experiments, $BaCl_2$ ignited in air	=137·428
II.	Three experiments, $BaCl_2$ ignited in HCl	=137·446
III.	Two experiments, $BaCl_2$ not ignited	=137·444
		137·439

From the Ratio of Baric Chloride to Silver.

I.	Five experiments, Stas's second method	=137·419
II.	Three experiments, first new method	=137·445
III.	Four experiments, second new method	=137·449
IV.	Two experiments, Stas's third method	=137·445
		137·440

Before discussing these averages it may be well to recall the results obtained from baric bromide. These last results may be divided into two groups of two series each, the essential difference between the two series depending upon their relative accuracy.

From the Ratio of Baric Bromide to Argentic Bromide.

I.	Experiments 3 to 12;	Ba=137·424
II.	Experiments 13 to 19;	Ba=137·439
		137·431

From the Ratio of Baric Bromide to Silver.

I.	Experiments 3 to 12;	Ba=137·422
II.	Experiments 13 to 19;	Ba=137·435
		137·428

Total average of four groups 137·434

The four groups, including eleven series and forty-nine individual results, are thus essentially unanimous in the verdict that the atomic weight of barium is between 137·42 and 137·45. Upon closer examination of details it is apparent that some of the series are more trustworthy than others. In general, the first series of each group is considerably less reliable than the following ones, for obvious reasons. The first series of the first and second groups have the additional disadvantage of having been the victims of rather unsatisfactory methods. Since the most probable errors tend in any case to lower the observed atomic weight, the striking out of these lower results appears all the more allowable.

The more trustworthy results which remain may be averaged as follows:—

From the ratio	$BaCl_2$	: 2AgCl ;	Ba	= 137·445
" "	$BaCl_2$	: Ag_2 ;	Ba	= 137·446
" "	$BaBr_2$	: 2AgBr;	Ba	= 137·439
" "	$BaBr_2$	: Ag_2 ;	Ba	= 137·435
		Average		137·441

This average is after all but little different from the total mean of all the determinations, 137·434; and either average may be taken without serious error for the atomic weight of barium. Indeed, in the present state of chemistry, the third decimal place is of little or no importance in a large atomic weight, and the round number 137·44 is sufficient for the most exacting work.

An excellent proof of the purity of the materials and the accuracy of the work is to be found in the comparison of the weights of silver and argentic chloride. Omitting in each case the less accurate first series, we may repeat the following figures:—

II. 2AgCl	:	$BaCl_2$ = 100	:	x = 72·6563
III. 2AgCl	:	$BaCl_2$ = 100	:	x = 72·6555
		Average..		72·6559
II. 2Ag	:	$BaCl_2$ = 100	:	x = 96·524
III. 2Ag	:	$BaCl_2$ = 100	:	x = 96·526
IV. 2Ag	:	$BaCl_2$ = 100	:	x = 96·524
		Average..		96·5247

Hence—

Ag : AgCl = 72·6559 : 96·5247
= 107·930 : 143·387

Therefore the atomic weight of chlorine is found to be 35·457, a quantity exactly identical with that found by Stas in a different way. A similar comparison of the weights of the silver and argentic bromide has been given already in the fifth column in the table on page 29 of the *Proc. Amer. Acad. Arts Sci.*, vol. xxviii.

It remains only to compare these figures with the older ones already described. Evidently all results for barium based upon the conversion of baric chloride into baric sulphate, as well as all results including water of crystallisation, are worthy of no confidence. The incomplete knowledge regarding the method of Gay-Lussac manifested by Marignac and Dumas in 1858 is quite enough to explain their unsatisfactory and discrepant results. We

should expect to find the ratio of baric chloride to argentic chloride the most accurately determined of all the old ratios; and, in fact, Turner in 1829 obtained in this way a very good result (137·45). Upon the other hand, Marignac's single result by this method (137·14) was much too low. The description of his work is so superficial that a guess as to the reason for this discrepancy is out of place; nor is such a guess necessary, for a single experiment can carry with it no important weight.

The new result for the atomic weight of barium, reduced to the various standards in present use, is given below. As before, the mathematical statement of the "probable error" is omitted, because this error is so small as to be meaningless.

If Oxygen	=	16·00,	Barium	=	137·44
,,	=	15·96,	,,	=	137·10
,,	=	15·88,	,,	=	136·41

ELEVENTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

The Committee on Indexing Chemical Literature presents to the Chemical Section its eleventh annual report.

During the past year the following bibliographies have been published:—

1. "Index to the Literature of Stereochemistry." By Arnold Eiloart. *Journ. Am. Chem. Soc.*, xiv., pp. 241—284.

This carefully prepared index also accompanies the author's "Guide to Stereochemistry" issued independently (New York, 1893). The material is arranged alphabetically by authors, with a chronological classification of publications and a special list of reviews.

2. "Index to the Literature of Explosives." Part 2. By Charles E. Munroe. Baltimore, 1893, pp. 43—195. 8vo.

This completes the undertaking begun several years ago by Professor Munroe; Part 1 was issued in 1886; twelve sets of periodicals embracing 984 volumes have been carefully examined.

3. "Materials for a Monograph on Inuline." By J. Christian Bay. *Trans. Acad. Sci.*, St. Louis, vi., 151 (1893). 9 pp. 8vo.

4. "Bibliography of the Tannoids." By J. Christian Bay. Fifth Ann. Report Missouri Botanical Garden (May, 1893). 27 pp. 8vo.

5. "Digest of the Studies on the Nature of the Organic Non-sugar in Saccharine Products." By J. A. Deghuée. *School Mines Q.*, xiii., pp. 313—334. (1893).

A subject-index followed by an author and title bibliography.

6. "Bibliography of Mineral Waters chronologically arranged." By Paul Schweitzer. Appendix C. Report on the Mineral Waters of Missouri. Vol. iii., *Geological Survey of Missouri*, December, 1892, pp. 237—244.

This is chiefly a translation of Osann's "Darstellung der bekannten Heilquellen," Berlin, 1829—43, with additions by Professor Schweitzer.

7. "A Bibliography of Analytical and Applied Chemistry for the Year of 1892." By H. Carrington Bolton. *J. Anal. Appl. Chem.* (1893).

8. "A Select Bibliography of Chemistry: 1492—1892." By Henry Carrington Bolton. Smithsonian Miscellaneous Collections, No. 850. Washington City, 1893. Pp. xvi.—1212. 8vo.

This work is the most extensive bibliography of chemistry hitherto published, yet it does not claim completeness; it contains 12,031 titles in twenty-four languages divided into seven sections, viz.:—I. Bibliography. II Dictionaries. III. History. IV. Biography. V. Chemistry, pure and applied, VI. Alchemy. VII. Periodicals. Appended to the section of Periodicals is a list of Abbreviations of the Titles of Chemical Periodicals, which is an extension of the list printed in the Fifth Annual Report of this Committee. A Subject-index of thirty pages, double columns, concludes this important work.

Reports of progress have been received from several chemists. Prof. J. Christian Bay, of the Missouri Botanical Gardens, St. Louis, Mo., whose published works are noticed above, is preparing a bibliography of alcoholic fermentation, with especial reference to vegetable physiology. He will be very glad to receive notes of the literature on this subject from botanists, chemists, and physiologists interested in having the bibliography as complete as possible.

Dr. Alfred Tuckerman expects to get ready for printing, during the coming year, that portion of his Bibliography of Mineral Waters which relates to the United States.

At a formal meeting of this Committee held in Rochester last August, it was voted to accept the following bibliography presented by Prof. A. B. Prescott, and to recommend it for printing to the Smithsonian Institution:—

"A Bibliography of Aceto-acetic Ester and its Derivations," including an Index of Literature on the subject. Compiled by P. H. Seymour, Assistant in General Chemistry, University of Michigan, June, 1892.

This work is now passing through the press, and will form one number of the Smithsonian Miscellaneous Collections.

Prof. H. W. Wiley will present to the Congress of Chemists at the Columbian Exposition the following communication:—

"A partial Bibliography of the Occurrence of Copper, Tin, Lead, and Zinc in Food and Drink, Vegetable and Animal Tissues, &c." By Mrs. Karl Thayer Pomeroy-McElroy.

This bibliography is styled partial because confined to only fifteen periodicals, which, however, are exhaustively indexed. It embraces nearly 1500 titles. The channel of publication is not yet determined.

The chairman of your committee will lay before the same Congress of Chemists a statement on bibliography, including a plan for an International Index to Chemical Literature; in this the work of this Committee is briefly set forth.

Respectfully submitted,

H. Carrington Bolton, Chairman,
F. W. Clarke,
Albert R. Leeds,
Alexis A. Julien,
John W. Langley,
Albert B. Prescott,
Alfred Tuckerman.

Advance proof sheets kindly communicated by Professor H. Carrington Bolton.

THE ESTIMATION OF PHOSPHORIC ACID.*

Preparation of Sample.

The sample should be well intermixed, finely ground, and passed through a sieve having circular perforations 1 m.m. in diameter. The process of grinding and sifting should take place as rapidly as possible, so that there should be no loss or gain of moisture during the operation.

Determination of Moisture.

(*a*) In potash salts, sodium nitrate, and ammonium sulphate, heat from 1 to 5 grms. at 130° until the weight is constant, and determine the loss in weight as moisture.

* Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (American) at its Meeting at Chicago, August, 1893.

(*b*) In all other fertilisers, heat 2 grms., or 5 grms. if the sample be very coarse, for five hours, at 100°, in a steam bath.

Methods of Determining Phosphoric Acid.

Water-soluble Phosphoric Acid.—Place 2 grms. in a 9 c.m. filter; wash with successive small portions of water, allowing each portion to pass through before adding more, until the filtrate measures about 250 c.c. If the filtrate be turbid, add a little nitric acid. Make up to any convenient definite volume; mix well; take any convenient portion and determine the phosphoric acid as under total phosphoric acid.

Citrate-insoluble Phosphoric Acid.—Heat 100 c.c. of strictly neutral ammonium-citrate solution of 1·0900 specific gravity to 65° C. in a flask placed in a bath of warm water, keeping the flask loosely stoppered to prevent evaporation. When the citrate solution in the flask has reached 65° C., drop into it the filter containing the washed residue from the water-soluble phosphoric-acid determination, stopper tightly with a smooth rubber stopper, and shake violently until the filter paper is reduced to a pulp. Place the flask back into the bath and maintain the water in the bath at such a temperature that the contents of the flask will stand at exactly 65° C. Shake the flask every five minutes. At the expiration of exactly thirty minutes from the time the filter and residue were introduced, remove the flask from the bath and immediately filter as rapidly as possible. Wash thoroughly with water at 65° C. Transfer the filter and its contents to a crucible, ignite until all organic matter is destroyed, add from 10 to 15 c.c. of strong hydrochloric acid, and digest until all phosphate is dissolved. Dilute the solution to 200 c.c. If desired, the filter and its contents can be treated according to methods 1, 2, or 3 under Total Phosphoric Acid. Mix well; filter through a dry filter; take a definite portion of the filtrate and determine phosphoric acid as under Total Phosphoric Acid.

In case a determination of citrate-insoluble phosphoric acid is required in non-acidulated goods it is to be made by treating 2 grms. of the phosphatic material, without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, &c.) the residue insoluble in ammonium citrate is to be treated by one of the processes described below under Total Phosphoric Acid 1, 2, or 3.

Total Phosphoric Acid.—In case of ignition the ignited material is to be dissolved in hydrochloric acid. Weigh 2 grms. and treat by one of the following methods:—(1) Evaporate with 5 c.c. of magnesium nitrate, ignite, and dissolve in hydrochloric acid. (2) Boil with 20 to 30 c.c. of strong sulphuric acid, adding 2 to 4 grms. of sodium or potassium nitrate at the beginning of the digestion and a small quantity after the solution has become nearly colourless, or adding the nitrate in small portions from time to time. A Kjeldahl flask graduated to 250 c.c. is recommended. After the solution is colourless, add 150 c.c. of water and boil for a few minutes, cool, and make up to volume. (3) Digest with strong sulphuric acid and such other reagents as are used in either the plain or modified Kjeldahl or Gunning methods for estimating nitrogen. Do not add any potassium permanganate, but after the solution has become colourless add about 100 c.c. of water and boil for a few minutes, cool, and make up to a convenient volume; 2·5 grms. of substance and a digestion flask graduated to 250 c.c. are recommended. [This method will be found convenient when both the nitrogen and the total phosphoric acid are to be determined in a fertiliser. In this case, after diluting to volume and mixing, a portion, for the estimation of nitrogen, may be removed with a pipette and the remainder then filtered through a dry filter and a portion taken for the determination of the total phosphoric acid.] (4) Solution in 30 c.c. of concentrated nitric acid with a small quantity of hydrochloric acid. (5) Add 30 c.c. of concentrated hydrochloric acid, heat, and add cautiously, in small quantities at a time, about 0·5 grm. of finely-pulverised potassium chlorate. (6) Solution in 15 to 30 c.c. of strong hydrochloric acid and 3 to 10 c.c. of nitric acid. This method is recommended for fertilisers containing much iron or aluminium phosphate. Boil until all phosphates are dissolved and all organic matter is destroyed; cool and dilute to 200 or 250 c.c.; mix and pass through a dry filter; take an aliquot part of the filtrate corresponding to 0·25 grm., 0·50 grm., or 1 grm., neutralise with ammonia, and clear with a few drops of nitric acid. (In case hydrochloric or sulphuric acid has been used as a solvent, add about 15 grms. of dry ammonium nitrate or its equivalent).

To the hot solutions, for every decigrm. of P_2O_5 that is present, add 50 c.c. of molybdic solution. Digest at about 65° C. for an hour, filter, and wash with water or ammonium-nitrate solution. Test the filtrate by renewed digestion and addition of more molybdic solution. Dissolve the precipitate on the filter with ammonia and hot water and wash into a beaker to a bulk of not more than 100 c.c. Nearly neutralise with hydrochloric acid, cool, and add magnesia mixture from a burette; add slowly (about 1 drop per second), stirring vigorously. After fifteen minutes add 30 c.c. of ammonia solution of density 0·95. Let stand for some time; two hours is usually enough. Filter, wash with dilute ammonia, ignite at white heat for ten minutes, and weigh.

Citrate-soluble Phosphoric Acid.—The sum of the water soluble and citrate insoluble subtracted from the total gives the citrate soluble.

Preparation of Reagents.

(1) *Ammonium-citrate Solution.*—(*a*) Mix 370 grms. of commercial citric acid with 1500 c.c. of water; nearly neutralise with commercial ammonia; cool; add ammonia until exactly neutral (testing with saturated alcoholic solution of corallin), and bring to volume of 2 litres. Test the specific gravity, which should be 1·0900 at 20° C., before using.

(*b*) *Alternate Method.*—To 370 grms. of commercial citric acid add commercial ammonia, sp. gr. 0·96, until nearly neutral; reduce the specific gravity to nearly 1·09 and make exactly neutral, testing as follows:—Prepare a solution of fused calcium chloride, 200 grms. to the litre, and add 4 volumes of strong alcohol. Make the mixture exactly neutral, using a small amount of freshly-prepared corallin solution as preliminary indicator, and test finally by withdrawing a portion, diluting with an equal volume of water, and testing with cochineal solution; 50 c.c. of this solution will precipitate the citric acid from 10 c.c. of the citrate solution. To 10 c.c. of the nearly neutral citrate solution add 50 c.c. of the alcoholic calcium-chloride solution, stir well, filter at once through a folded filter, dilute with an equal volume of water, and test the reaction with neutral solution of cochineal. If acid or alkaline, add ammonia or citric acid, as the case may be, mix, and test again, as before. Repeat this process until a neutral reaction is obtained. Bring to the proper specific gravity of 1·0900 at 20° C.

(2) *Molybdic Solution.*—Dissolve 100 grms. of molybdic acid in 400 grms. or 417 c.c. of ammonia, sp. gr. 0·96, and pour the solution thus obtained into 1500 grms. or 1250 c.c. of nitric acid, sp. gr. 1·20. Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment and preserve in glass-stoppered vessels.

(3) *Ammonium Nitrate Solution.*—Dissolve 200 grms. of commercial ammonium nitrate in water and bring to a volume of 2 litres.

(4) *Magnesia Mixture.*—Dissolve 22 grms. of recently ignited calcined magnesia in dilute hydrochloric acid, avoiding an excess of the latter. Add a little calcined magnesia in excess, and boil a few minutes to precipitate iron, alumina, and phosphoric acid; filter; add 280 grms. of ammonia chloride, 700 c.c. of ammonia of sp. gr.

0·96, and water enough to make a volume of 2 litres. Instead of the solution of 22 grms. of calcined magnesia, 110 grms. of crystallised magnesium chloride ($MgCl_2$, $6H_2O$) may be used.

(5) *Dilute Ammonia for Washing.*—One volume of ammonia, sp. gr. 0·96, mixed with 3 volumes of water, or usually 1 volume of concentrated ammonia with 6 volumes of water.

(6) *Nitrate of Magnesia.*—Dissolve 320 grms. of calcined magnesia in nitric acid, avoiding an excess of the latter; then add a little calcined magnesia in excess; boil; filter from the excess of magnesia ferric oxide, &c., and bring to volume of 2 litres.

REPORT OF COMMITTEE ON DETERMINATIONS OF ATOMIC WEIGHT PUBLISHED DURING 1893.*

By F. W. CLARKE.

The Committee, appointed at the last annual meeting, respectfully submits the following report, showing the advances made in our knowledge of atomic weights during 1893. The year has been one of reasonable activity in this branch of investigation, and it is thought that all the work actually published within its limits is here summarised and recorded. One partial exception possibly may be made to this statement. Morley's work on oxygen, reported orally at the American Association meeting, and at the Chemical Congress in Chicago, is omitted, for only unofficial abstracts of it have yet appeared in print. That work is of such fundamental importance that it seems best to await its completion, rather than to do it possible injustice by fragmentary notices which might be inexact.

In the "Stas Memorial Lecture," by Professor Mallet (*Journ. Chem. Soc.*, August, 1893), will be found a remarkably full discussion of the theory or philosophy of atomic weight determinations, which should be carefully read by all students in this domain. Taking the life and work of Stas as text and example, Mallet considers the conditions necessary to the fruitful continuation of that work, and throws out many suggestions of great practical value. He particularly advocates the multiplication of interdependent data, in order that errors may be eliminated; and he also recommends the establishment of a special endowed laboratory, in which a group of trained observers may co-operate towards the attainment of the best results.

The individual atomic weight determinations of 1893 are subjoined.

Boron.

W. Ramsay and Emily Aston (*Journ. Chem. Soc.*, lxiii., 207, February, 1893) re-determine the atomic weight of boron by two distinct processes; one of them being entirely new. First, with many precautions, they estimate the percentage of water in crystallised borax, $Na_2B_4O_7,10H_2O$; all weights being reduced to vacuum standards. The same reduction is also made in their other series, but as they carry out the weights to seven decimal places, the corrections applied go further than is necessary. In the subjoined tables I give the nearest tenth m.grm.

Weight $Na_2B_4O_7,10H_2O$.	Weight $Na_2B_4O_7$.	Per cent H_2O.	At. wt. B.
10·3582	5·4784	47·1099	11·04
5·3440	2·8247	47·1433	10·97
4·9963	2·6379	47·2026	10·85
5·7000	3·0101	47·1912	10·87
5·3143	2·8066	47·1882	10·88
4·9972	2·6392	47·1865	10·885
5·2367	2·7675	47·1524	10·955

Mean atomic weight, B = 10·921, ±0·010.

* From the *Journal of the American Chemical Society*, xvi., No. 3.

In the second series of experiments fused borax was distilled with hydrochloric acid and methyl alcohol, and the residual sodium chloride was weighed. Results as follows:—

Wt. $Na_2B_4O_7$.	Wt. NaCl.	At. wt. B.*
4·7684	2·7598	11·015
5·2740	3·0578	10·925
3·2344	1·8727	10·992
4·0862	2·3713	10·879
3·4970	2·0266	10·949

Mean atomic weight, B = 10·952, ±0·010.

* Atomic weights used in Ramsay and Aston's calculations:—O=16, H=1·008, Ag=107·92, Na=23·05, Cl=35·45, and Br=79·95.

The distillations were conducted in soft glass flasks of about 100 c.c. capacity, in which the sodium chloride was dried at about 350°, and finally weighed. It was found, however, that the flasks were somewhat attacked during the process, with liberation of silica, consequently some oxygen in the alkali of the glass had been replaced by chlorine, and the weight of the vessel increased. Another set of distillations was, therefore, made with flasks of hard combustion-tubing, and these were slightly attacked also.

Wt. $Na_2B_4O_7$.	Wt. NaCl.	At. wt. B.
5·3118	3·0761	10·983
4·7806	2·7700	10·955
4·9907	2·8930	10·936
4·7231	2·7360	10·968
3·3138	1·9187	10·992

Mean atomic weight, B = 10·966, ±0·005.

As a check upon these results the sodium chloride was dissolved in water, and after filtration precipitated with silver nitrate. The resulting silver chloride was collected on a Gooch filter, dried at 200° and weighed.

Wt. AgCl.	P.c. Cl in NaCl.	At. wt. B from Cl.
7·5259	60·493	11·071
6·7794	60·515	11·024
7·0801	60·516	11·003
6·6960	60·514	11·039
4·6931	60·479	11·091

Mean atomic weight, B = 11·052, ±0·010.

From all these results, and after discussing the supposable sources of error in them, the authors conclude that the atomic weight of boron is very nearly eleven.

Still another determination of the atomic weight of boron, by an entirely independent method, is due to Rimbach (*Ber. d. Chem. Ges.*, xxvi., 164, Feb. 13, 1893). Taking advantage of the fact that methyl orange, as an indicator, is unaffected by free boric acid, he titrated solutions of borax with standardised hydrochloric acid, thus measuring the amount of sodium in the salt and thence calculating the value to be ascertained. The borax was prepared in platinum vessels from carefully purified boric acid and sodium carbonate; and the hydrochloric acid used contained 1·84983 per cent of absolute HCl, determined gravimetrically as silver chloride. In the following table of results the titrated hydrochloric acid is given by weight in grammes:—

Wt. Borax.	Wt. HCl sol.	Per cent Na.*	At. wt. B.*
10·00214	103·1951	12·07081	10·9646
15·32772	158·1503	12·07138	10·9598
15·08870	155·7271	12·07530	10·9273
10·12930	104·5448	12·07517	10·9298
5·25732	54·2571	12·07435	10·9361
15·04324	155·2307	12·07283	10·9486
15·04761	155·2959	12·07448	10·9356
10·43409	107·6602	12·07176	10·9571
5·04713	52·0897	12·07480	10·9330

* Calculations made with O=16, H=1·0032 (Keiser), Na=23·0573, Cl=35·4529, and Ag=107·9376.

Calculating from the sum of all the weights the atomic weight of boron becomes 10·945, ±0·003.

Carbon.

Leduc (*Comptes Rendus*, cxv., 1072) has determined the density of carbon monoxide, deducing thence the atomic weight of carbon. The globe used held 2·9440 of air. Filled with carbon monoxide the latter weighed—

2·8470
2·8468
2·8469

Mean 2·8469

Hence the density of CO is 0·96702, when air = 1, and with—

O = 15·88
C = 11·913,

If O = 16, then C = 12·003.

In a very brief note (*Phil. Mag.*, 5, xxxvi., 552, Dec., 1893) Wanklyn announces that he has studied a series of hydrocarbons in which the successive steps rise—not by $CH_2 = 14$—but by ½ $(CH_2) = 7$. If these observations are sustained, then the atomic weight of carbon becomes = 6.

Cobalt and Nickel.

Atomic weights determined by Winkler (*Zeit. Anorg. Chem.*, iv. 10, 1893), who starts with weighed quantities of metal, electrolytically deposited. This is then dissolved in a platinum dish in pure hydrochloric acid, and the chlorides produced are finally dried for several hours at 150°. In one set of experiments the chlorine in the chlorides is weighed gravimetrically, as silver chloride; in another set it is titrated with a standard solution of silver. In the first case we have the ratio R : 2AgCl; in the other, R : Ag_2. Results as follows, for nickel:—

Wt. Ni.	Wt. AgCl (grav.)	At. wt. Ni.
0·3011	1·4621	58·9102
0·2242	1·0881	58·9418
0·5166	2·5108	58·8571
0·4879	2·3679	58·9419
0·3827	1·8577	58·9304
0·3603	1·7517	58·8334

Mean result, Ni = 58·9033.

Wt. Ni.	Wt. Ag (vol.)	At. wt. Ni.
0·1812	0·6621260	58·9253
0·1662	0·6079206	58·8665
0·2129	0·7775252	58·9584
0·2232	0·8162108	58·8811
0·5082	1·8556645	58·9684
0·1453	0·5315040	58·8631

Mean result, Ni = 58·9104.

The following data were obtained for cobalt:—

Wt. Co.	Wt. AgCl (grav.).	At. wt. Co.
0·3458	1·6596	59·6044
0·3776	1·8105	59·6609
0·4493	2·1521	59·7215
0·4488	2·1520	59·6577
0·2856	1·3683	59·7081
0·2648	1·2678	59·7480

Mean result, Co = 59·6834.

Wt. Co.	Wt. Ag (vol.).	At. wt. Co.
0·177804	0·6418284	59·6495
0·263538	0·9514642	59·6396
0·245124	0·8855780	59·5996
0·190476	0·6866321	59·7311
0·266706	0·9629146	59·6388
0·263538	0·9503558	59·7092

Mean result, Co = 59·6613.*

* All calculations with Ag = 107·66 and Cl = 35·37.

In the case of the cobalt determinations it is of course conceivable that the chloride formed might be contaminated with traces of basic compounds. This question is considered by Winkler in a supplementary communication (*Zeit. Anorg. Chem.*, iv., 462, 1893). The weighed electrolytic cobalt deposited upon the surface of the platinum dish was treated with a solution of neutral silver sulphate. Silver was thrown down, and was washed, dried, ignited, and weighed. Thus a direct ratio was measured between silver and cobalt, involving no intervention of cobalt chloride, and consequently no error due to basic salts. Results as follows:—

Wt. Co.	Wt. As.	At. wt. Co.
0·2549	0·9187	59·7421
0·4069	1·4691	59·6377

The precipitated silver, as a check upon its purity, was dissolved in nitric acid, re-precipitated with hydrochloric acid as chloride, and filtered off. The filtrate, upon evaporation to dryness, gave traces of residue, containing cobalt. The amount of the latter in the first experiment was at most 0·5 m.grm., and in the second not over 0·2 m.grm. Correcting for these amounts, the values found for the atomic weight of cobalt become 59·6356 and 59·6164 respectively. These figures fall within the limits of variation of those found in the first paper, and show that the supposed error, if it existed, could not be large. The author admits, however, that the degree of concordance among his experiments is not so great as could be desired. The main purpose of his work was to show the essential constancy of the values, as opposed to the views of Krüss concerning the supposed composite nature of nickel and cobalt.

Molybdenum.

Atomic weight re-determined by Smith and Maas (*Journ. Am. Chem. Soc.*, xv., 397, July, 1893; results calculated with O = 16, Na = 23·05, and Cl = 35·45). Sodium molybdate was converted into chloride by heating in a current of pure dry gaseous hydrochloric acid. Results as follows with weights reduced to vacuum standards:—

Wt. Na_2MoO_4.	Wt. NaCl.	At. wt. Mo.
1·14726	0·65087	96·130
0·89920	0·51023	96·094
0·70534	0·40020	96·108
0·70793	0·40182	96·031
1·26347	0·71695	96·087
1·15217	0·65367	96·126
0·90199	0·51188	96·067
0·81692	0·46358	96·077
0·65098	0·36942	96·073
0·80563	0·45717	96·078

In mean, Mo = 96·087.

(To be continued.)

NOTICES OF BOOKS.

The Alchemical Essence and the Chemical Element. An Episode in the Quest of the Unchanging. By M. M. PATTISON MUIR. London and New York: Longmans, Green, and Co. 8vo., Pp. 94.

THIS work contrasts the elements of modern chemistry with the essences dealt with by those interested but bewildered and bewildering workers and thinkers, the alchemists. In their works we read, *e.g.*, of mercury and sulphur. But their mercury and sulphur were not the elements which we now understand by those names. Their sulphur was the principle of changeability, and their mercury was the principle of malleability and lustre. Both these substances—if substances they may be called—were, as Mr. Pattison Muir well puts it, "in-

tellectual abstractions clothed in material garments which fitted very loosely and were constantly being put off and on."

Our concept of an element, as a something to which we may add, but from which at present we can take nothing away, was as little reached by the alchemists as by the old Greek philosophers with their fire, air, earth, and water.

"The properties of metals," says Mr. Muir, "were considered by the alchemists to depend not only on the quantities of mercury and sulphur they contained, but also on the purity of the mercury and sulphur and on the degree of fixation of these in the metals." This is as fair a rendering of the alchemical ideas as is practicable. But it is hard for us to understand what the alchemists meant by purity and fixity. Our author thinks that they conceived of all things save *The One Thing* as slowly growing, changing, developing, and coming to maturity, and that they firmly believed in the quest of *The One Thing* which was the master-key of all mutations." But we can scarcely venture to identify their *One Thing* with the ὑλη of Roger Bacon, or to consider their constant mutability as a foreshadowing of our evolution.

Mr. Muir shows that whilst alchemy in its cruder aspect was an unsuccessful attempt at gold-making, in its higher phase it was a mystical system of occult theology. He complains, fairly enough, that there are in our days men who stand on the same "plane" as the alchemists, without their excuse. Formerly we had to encounter the old utilitarian; we have now to deal with neo-utilitarians, ethicists, theosophists, &c., who fancy that they are seeking an explanation of material facts on a "higher spiritual plane;" in other words, in the attics of a "chateau en Espagne."

The reader will find in Mr. Muir's treatise a clearer explanation of Alchemy than he could hope to obtain from the original documents of Paracelsus, Lully, or Tritheim.

Science Progress; a Monthly Review of Current Scientific Investigation. Vol. I., No. 1. London: Scientific Press, Limited.

Science progress? *The* progress which is genuine and which cannot be compared to the rogue's march to the gallows or the sick man's journey to the church-yard. We have every reason to congratulate our new contemporary on its appearance and to wish it an ample measure of success.

As far as we can judge from the prospectus offered by the Editorial Committee and from the spirit of the articles *Science Progress* will concern itself with pure Science and not with that medley which is belauded by some and denounced by others under the name of Science. It will be an organ, not of appliers and projectors, but of discoverers and—if we may use the modern barbarism—of researchers. It seeks, as is especially shown in the opening article by Prof. G. F. Fitzgerald, to call attention to the mutual bearings of the several sciences and the light which they throw, or may be made to throw, upon each other. Questions are raised which require trains of experiment for their solution and which will in any case prove fruitful. A road between physics and biology is desired and will be most valuable. But its pioneers must beware lest they are lost in the Serbonian bog which entombed Borelli, Sanatorius, and the rest of the iatromathematicians.

We are reminded that the work done in physical science in innumerable laboratories should be collected, digested, and distributed. "An undue development of specialisation without sufficient nourishment and communication from other parts" is mentioned as a peril to be shunned. Who can help uttering an involuntary *cui bono* when he reads of endless organic compounds discovered and analysed? Leaving possible industrial applications on one side, is the only outcome of all this activity to be a collection of long names and of *Lagerungs* formulæ?

Many of the papers in *Science Progress* will be difficult of assimilation by readers who may fairly rank as men of science, but whose specialty lies in a different direction. We should therefore suggest that in such cases the result aimed at and the result actually reached might be advantageously shown at the end of each article.

Finally, we must wish *Science Progress* readers fit, but not few.

An Introduction to the Organic Compounds of Every Day Life. By Julius T. Willard, Assistant Professor of Chemistry, Kansas State Agricultural College, Manhattan, Kansas. 1894. (Publisher's name not given).

This book, which bears outside the general title "Organic Chemistry," reminds us in some respects of Johnston's "Chemistry of Daily Life," or of G. H. Lewes's "Physiology of Daily Life." It is, however, more technical and less readable than either of the above works. No one will deny the use of graphic formulæ to the chemist; but in a work like that of Mr. Willard, which addresses the outsider, they seem decidedly out of place. It will be an evil day when the high explosives can legitimately figure as organic compounds of every day life. Hence we regret that Mr. Willard has given them so much of his space. The cyanides, on the contrary, receive little attention, as is also the fate of the amido compounds.

We are not sorry to notice that Mr. Willard in his introduction cautions his readers that they must never hope to pass "from the organic to the organised."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 13, March 27, 1894.

Study of the Crystalline Barium and Strontium Acetylides.—Henri Moissan.—The coke crucible of the electric furnace is filled with an intimate mixture of 50 grms. anhydrous baryta and 30 grms. carbonised sugar. It is heated from 15 to 20 minutes with a current of 350 amperes and 70 volts. When cold it is a black brittle mass, of the composition C_2Ba. The strontium carbide is obtained with the same ease and under the same conditions as the barium compound. The barium compound is the most fusible of the alkaline earthy carbides, and has the specific gravity 3·75. The density of the strontium carbide is 3·19. Both these compounds are at once decomposed on contact with water, yielding hydroxide and pure gaseous acetylene. With the hydracids their reaction is very energetic, amounting in case of hydrochloric acid to incandescence.

On Two Isomeric Methyl-cyano Camphors.—MM. A. Haller and Minguin.—The α compound is a thick yellowish liquid of the rotatory power $(\alpha)_0 = +90°1°$, and which sometimes deposits soft, yellow crystals fusible between 38° and 45°, and having the same composition and rotatory power as the liquid on which they are formed. The body α behaves like the cyano-camphor itself and yields with alcoholic potassa methyl-hydroxy-campho-carbonic acid. The isomer β behaves like certain mixed ethers of phenols which are saponified both by acids and alkalis.

Mutual Solubility of Salts.—H. Le Chatelier.—According to the author the determination of the mutual solubility of salts comprises three distinct cases:—1. The

case where the two salts solidify together, forming isomorphous mixtures of variable composition. 2. The case where the two salts solidify separately. 3. The case where the two salts may form a definite compound. The author gives his results for the second case in the form of a diagram.

Action of Nitrogen, Nitrous, and Nitric Oxides upon the Alkaline Ammoniums.—A. Joannis.—Nitrogen does not decompose the alkaline ammoniums. The action of nitrous oxide upon sodammonium and potass-ammonium is complex. If the supply of the gas is stopped when the ammonium is decolourised we find that (1) the volume of nitrogen evolved is approximately equal to the volume of nitrous oxide employed; (2) that for each mol. of sodammonium there disappears rather more than a mol. of nitrous oxide; (3) that ammonia is always at the same time fixed upon the substance; (4) the product obtained disappears in the water without an evolution of gas; (5) the solution gives with silver nitrate a violently explosive compound, N_3Ag.

Journal fur Praktische Chemie.
Vol. xlix., Part 4, 1894.

Relations between the Refractive and Rotatory Power of Chemical Compounds, and on a New Method of Determining the Specific Rotation of Optically Active Substances.—J. Kanonnikoff.—The results of this investigation are shown in a series of fourteen tables.

On Oil of Roses.—J. Bertram and E. Gildemeister.—The author gives a comparative view of German, Turkish, Bulgarian, and French oil of roses, including also the geranium oil from *Andropogon schœnanthus*, erroneously known formerly as Turkish geranium oil, African geranium oil from Algiers, &c.

Action of Nitrous Acid upon Acetylglutaric Ester.—G. Baldracco.—The author has examined acetylglutaricdiethyl ester, γ-isonitroso-acetobutyric acid and the behaviour of the former with phenylhydrazine and hydroxylamine.

Formula of the so-called Oxybrassidic Acid (Ketobehenic Acid.—M. Filetti.—The acid described by Holt and Baruch has not the formula $C_{22}H_{40}O_3$, but $C_{22}H_{42}O_3$.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., No. 4.

Study on the Ebullioscope and its Use for Determining Alcohol in Beers.—H. Tornöe.—The instrument used differs only in detail from that invented by Vidal and Maligand. The movable centesimal scale is replaced by a graduation in centigrade degrees etched on the stem of the thermometer. This modification admits of a strict compensation of errors in the calibre of the thermometer. The author gives a table showing the fall of the boiling-point in proportion to the weight of alcohol in 100 parts of water.

Action of Sulphuric Acid upon Wood Charcoal.—A. Verneuil.—Already inserted.

On Ethl-allyl-carbinol.—H. Fournier.—This compound, $C_6H_{12}O$, is a colourless liquid, of an agreeable odour, of the sp. gr. 0·891 at 18°. Its boiling-point lies between 150° and 152°.

On Chloralose.—A. Petit and M. Polowowski.—In 1889 Heffter detected two new products obtained by the action of chloral anhydride upon glucose. The two products have the same formula, $C_8H_{11}Cl_3O_6$, and differ from each other merely by the physical properties and those of their derivatives. The more soluble of the two is distinguished by its poisonous character.

Stereoisomers in the Camphor Series.—L. Bouveault.—This memoir does not admit of useful abstraction.

On Optical Isomerism in Substances with Closed Chains.—L. Bouveault.—Not suitable for abstraction.

On Caseine and its Organic Phosphide.—A. Béchamp.—This paper is too lengthy for insertion.

Formation of Mannite in Wines.—H. and A. Malbot.—A continuation from the foregoing issue.

Zeitschrift fur Analytische Chemie.
Vol. xxxii., Part 6.

Wine Statistics of Germany.—This memoir would have no especial interest for our readers.

An Attempt at the Simultaneous Determination of Carbon, Nitrogen, and Hydrogen.—Dr. Hans Malfatti.—This paper will be inserted at some length.

The Recognition of Nitrites in Urine.—Dr. Adolf Jolles.—The reaction with dilute sulphuric acid and potassium iodide with starch paste is very sensitive in water, but in urine it is not sufficiently sensitive, since both normal and pathological constituents of urine take part in the absorption of iodine, and interfere with the reaction to a greater or less degree, and in the case of small traces entirely. The most suitable reagent for nitrites in urine is sulphanilic acid and α-naphthylamine sulphate. The lowest limit is 0·000032 grm., N_2O_3 in 100 c.c. of urine. For the qualitative recognition of nitrites in urine "Schäffer's test" (potassium ferrocyanide with acetic acid) is suitable. The lowest limit is 0·000045 grm. N_2O_3 in 100 c.c. urine. For the quantitative petermination the test in urine according to Devanter's procedure is unsuitable. For an approximate quantitative determination of nitrites in urine Trommsdorff's colorimetric method is exclusively available.

MISCELLANEOUS.

Electrolytic Treatment of Sewage.—The Hermite process has received an exhaustive trial at Worthing. The Medical Officer of Health says in his official report: "Since there is no instantaneous decomposition of fæcal matter, and no sterilisation of the sewage, I am of opinion that the process, as far as the late trials have gone, has therefore failed to produce for it the results which are claimed for it by its inventor."

Antitoxin for Diphtheria.—Hans Aronson (*Chemiker Zeitung*).—The author shows that dogs are remarkably susceptible to diphtheria, but that from the serum of their blood a principle can be obtained which confers immunity on other animals and on human beings. The immunisation of children threatened with diphtheria is now possible in medical practice. A solution of the serum is produced by the Company formerly E. Schering.

Jena Utensil-Glass.—We have received from Messrs. Baker and Co., Holborn, a sample beaker of this glass, and have submitted it to some severe tests, with the result of showing that it is undoubtedly as good as its makers claim. We first filled the beaker with cold water, and, without drying it on the outside, placed it over a naked Bunsen flame. When the contents boiled it was quickly emptied and plunged into cold water. Then, wet as it was (but empty), it was again placed over the flame, where it was left till dry (and naturally considerably above 100° C.). It was then plunged into cold water a second time, and it still remained unharmed. Such results speak for themselves, and we must congratulate the manufacturers on their success.

Chemical Instruction in Germany.—The *Chemiker Zeitung* has been giving a summary of the arrangements for the study of chemistry and the allied sciences for the summer term at the Universities and Technical High Schools of Germany, Austria, and Switzerland. It will be seen that in the last-named country, which certainly does not exceed some English counties in the extent of its resources, there are universities, *i.e.*, Basle, Bern, Geneva, Lausanne, Nauchatel, and Zurich, besides the important technical High School of Zürich. If we look at one of the less celebrated and less wealthy universities of Germany, *e.g.*, Würzburg, we find the following professional staff:—Fick, physiological investigations; Fick and Gürber, chemico-physiological exercises; Lehmann, hygiene, hygienic excursions, course of bacteriology, work in the hygienic laboratory for advanced students; Schenck, exercises in metabolism and nutrition, physiological practicum; von Sandberger, geology, geological exercises and excursions, introduction to independent research; von Sachs, natural history of the vegetable kingdom, exercises in microscopy; Prym, integral calculus; Röntgen, experimental physics and practical work in the physical laboratory; Hantzsch, organic and experimental chemistry; Wislicenus, volumetric analysis; Tafel, select chapters in physical chemistry; Hantzsch and Wislicenus, practical work in the general and in the analytical laboratory; Hantzsch, Wislicenus, and Tafel, guidance to original research; Selling, electro-magnetism and theory of light; Medicus, chemical technology, and practice in all departments of applied chemistry; Geigel, theoretical optics; Wien, theory of heat. At some universities there are special courses in toxicology (chemical and microscopical), and in forensic chemistry. At others there is special instruction and practice in spectroscopy. At none is time and brain-power spent in "preparing for exams.," and no funds are squandered in paying examiners.

MEETINGS FOR THE WEEK.

MONDAY, 16th.—Society of Arts, 8. (Cantor Lectures). "Photometry," by Capt. W. de W. Abney, C.B., F.R.S.
—— Medical, 8.30.
TUESDAY, 17th.—Royal Institution, 3. "Electric Illumination," by Prof. J. A. Fleming, F.R.S.
—— Institute of Civil Engineers, 8.
—— Pathological, 8.30.
WEDNESDAY, 18th.—Society of Arts, 8. "Design Applied to Carpets," by Alexander Millar.
—— Meteorological, 8.
—— Microscopical, 8.
THURSDAY, 19th.—Royal, 4.30.
—— Royal Institution, 3. "Music—I. Musical Gestures" (with Musical Illustrations), by Prof. J. F. Bridge, Mus.Doc.
—— Society of Arts, 8. "Tasmania and the Forthcoming Hobart International Exhibition, 1894—95," by G. Collins Levey, C.M.G.
—— Chemical, 8. "Action of Metals on Strong Acids," by G. J. Burch, M.A., and J. W. Dodgson. "Action of Light on Oxalic Acid," by Dr. A. Richardson. "English Jute Fibre. II." by A. Pears, jun. "Natural Oxycelluloses," by C. Smith.
(By a regrettable printer's error this meeting was incorrectly announced in our last issue as being held on the 12th instead of the 19th inst.).
FRIDAY, 20th.—Royal Institution, 9. "Early British Races," by John G. Garson, M.D.
—— Quekett Club, 8.
SATURDAY, 21st.—Royal Institution, 3. "Literature and Journalism," by H. D. Traill, D.C.L.

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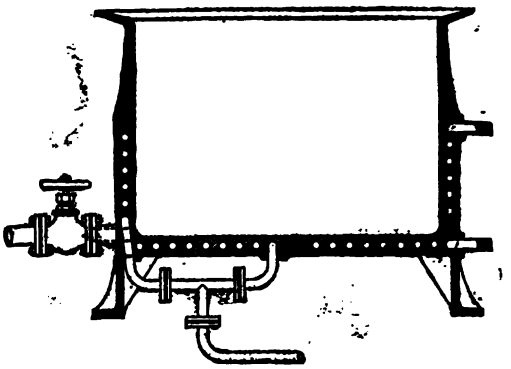

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says:—

P. 316. "An improved vessel for boiling oil, and suitable for many other kindred purposes, has been recently described by T. Frederking (CHEMICAL NEWS, London). A coil of stout piping is arranged in a casting mould, so that the molten metal forming the pan is cast round the coil, much as is done in the case of the water-tuyeres of a blast furnace. Steam at any pressure [or any other heating medium] being passed through the coil, the pan is heated up proportionately without any danger, the pressure bearing solely on the piping and not on the metal pan itself, whilst the well conducting metal walls allow the heat to pass readily. Temperatures up to 350° and 400° C. can be thus obtained."

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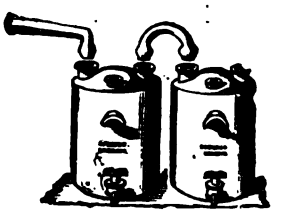

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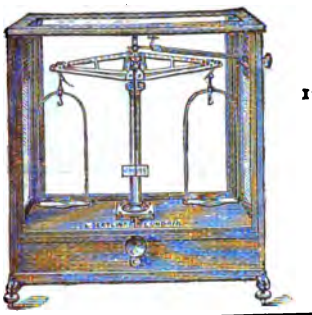

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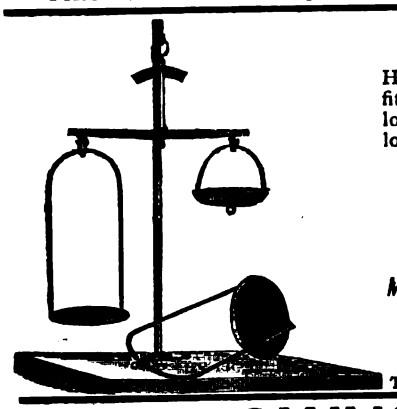

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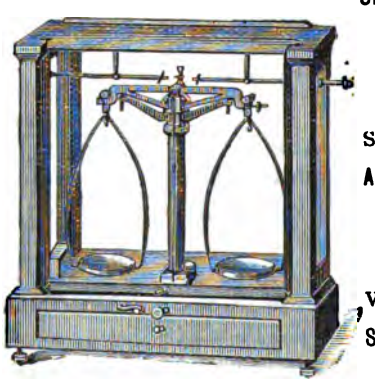

FIG. 3*a*.

SHORT BEAM BALANCE, No. 10*a*, Fig. 3*a*, to carry 100 grammes in each pan, and turn to 1-10th milligrm. Steel knife-edges, agate planes, two rider apparatus, and new improved arrangement for arrest of pans £8 15 0
Same with agate knife-edges £9 15 0

ANALYTICAL BALANCE, No. 7, to carry 50 grammes and turn to 1-5th milligramme. Steel knife-edges, agate planes, one rider apparatus, and new improved arrangement for arrest of pans £6 10 0
With agate knife-edges .. £7 10 0

STUDENT'S BALANCE, No. 69, to carry 30 grammes and turn to ½ milligramme £2 10 0

BALANCE No. 28, to carry 50 grammes and turn to ½ milligramme £2 16 8

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THE CHEMICAL NEWS.

Vol. LXIX., No. 1795.

PREPARATION AND PROPERTIES OF CARBON BORIDE.

By HENRI MOISSAN.

In the action of the electric arc upon boron, silicon, and carbon, we have previously drawn attention to the existence of novel crystalline compounds, produced at a very high temperature, possessing such stability that they are not attacked by most of our reagents, and being so hard as to be near to, equal, or even superior to the diamond. We have already given several processes for the preparation of carbon silicide, and we now describe a new similar compound—carbon boride.

In 1857 Deville and Woehler pointed out the existence of a variety of boron, to which they gave the name adamantine boron. Hampe, repeating this experiment, demonstrated that we had to do with a mixture of compounds containing in particular an aluminium boride and carboboride, both definite and crystalline.

In more recent researches on the same subject, Joly has isolated in this mixture a small quantity of a carbon boride, in which the determination of the carbon, after treatment with chlorine, led to the formula Bo_6C.

If we cause boron to react upon carbon at the temperature of the electric furnace, there are formed two borides, one stable and the other attackable by a mixture of potassium chlorate and nitric acid. The former has the composition Bo_6C, and forms the subject of the present memoir.

This carbon boride may be produced—

1. If we cause the arc to play between two carbons agglomerated by means of a mixture of boric acid and carbon silicide. Under these conditions it is always contaminated with carbon silicide.

2. If we place a small quantity of boron in the midst of the electric arc.

3. If we heat to 3500° in the electric furnace, pure boron in a small carbon crucible fitted with its lid.

4. This boride is also formed in the midst of melting metals. It is produced if we heat in the electric furnace in a crucible of carbon an iron boride rich in boron. The melted regulus is attacked, first with hydrochloric acid, then with aqua regia, when there separates out a black residue of graphite and carbon boride.

If in this experiment we use siliceous cast-iron, the residue obtained after treatment with the acids is formed of a mixture of carbon boride and carbon silicide.

5. On submitting a mixture of carbonised sugar and pure boron to the solvent action of silver and copper, heated in the electric furnace. In this case there are produced very definite crystals of carbon boride.

1. *Preparation by the Direct Union of Boron and Carbon.*—We heat in a crucible of coke in the electric furnace a mixture of 66 parts of amorphous boron and 12 parts of carbonised sugar. The current employed measures 250 to 300 ampères and 70 volts. The reaction is complete in six to seven hours.

After the crucible is cool we collect a black mass of a graphitoid aspect and a brilliant fracture, presenting an incipient fusion. After prolonged treatment with fuming nitric acid the substance is disaggregated, and there remains a crystalline powder, which is subjected to six treatments with potassium chlorate and monohydrated nitric acid. It is washed with water and dried.

2. *Preparation by Solution in Iron Boride.*—Iron combines readily with boron, producing definite borides which we shall describe subsequently. On adding to iron an excess of boron and carbon, and heating the whole in the electric furnace under the conditions described above, there is formed an ingot with a very brilliant fracture. After treatment with aqua regia the metal leaves a residue consisting almost entirely of carbon boride. In this case the crystals are ill-defined; after six treatments with potassium chlorate it contains no graphite, and its composition is Bo_6C.

3. *Preparation by Solution in Copper and in Silver.*—As iron readily dissolves a notable excess of boron, we have sought to employ in this preparation metals which at the moment where they refrigerated, do not form definite combinations with boron. Silver, and especially copper, have yielded better results.

The carbon boride obtained in silver, after treating this metal with nitric acid, is very pure, but its crystallisation is confused. With copper we obtain very well-defined brilliant crystals.

We prepare an intimate mixture of boron and charred sugar as above directed, and put 15 grms. of this mixture in a carbon crucible with 150 grms. of coarse filings of very pure copper.

The mixture is heated from six to seven minutes with a current of 350 ampères and 70 volts. A few moments afterwards we extract from the furnace a malleable ingot which has preserved the appearance of metallic copper, though slightly blackened on the surface. The fusion is effected very rapidly; it is easy to obtain in three hours the quantity of copper ingots necessary for the preparation of about 200 grms. carbon boride.

A simple treatment with common nitric acid enables us to obtain the boride very well crystallised and containing only a small quantity of graphite. To eliminate this latter body the mixture is treated from six to eight times with dry potassium chlorate and concentrated nitric acid. It is then treated for some hours with boiling sulphuric acid. Lastly, it is digested anew with the mixture of chlorate, washed, and dried.

Properties.—This carbon boride belongs to the same class of compounds as carbon silicide. Like the latter it is very stable and hard. It appears in black brilliant crystals of specific gravity 2·51.

Chlorine attacks it below 1000° without incandescence. There is formed a boron chloride, and there is left a residue of porous and very brilliant carbon. Bromine and iodine have no action.

If heated in oxygen to 500° it does not produce carbonic acid, but at 1000° it burns slowly, less easily than diamond, yielding carbonic acid and a black residue coated with melted boric acid.

Sulphur does not react upon carbon boride at the temperature at which glass softens. It is the same with phosphorus and nitrogen at 1200°. This compound is not attacked by any acid. Concentrated hydrochloric acid, monohydrated nitric, or their mixture, do not attack it at ebullition. If heated to 150° in a sealed tube for four hours, it gives off nothing to fuming nitric acid. Concentrated solutions of iodic and chromic acids are also without action at ebullition or at 150° in sealed tubes.

At a dull red heat it is attacked by melting potassa and by a melting mixture of potassium and sodium carbonates. The most interesting character of this novel compound is its extreme hardness. Whilst with carbon silicide we can scarcely polish diamond, but not cut it, with the dust of carbon boride we can produce facets upon a diamond.

This compound is very friable. We can obtain it in fine powder in a new Abich mortar, mix it with oil, and make use of it on the mill for cutting diamond.

Determination of the Carbon.—We have obtained in its analysis: Boron 84·57, 84·19, and 84·52 per cent; and carbon 15·6, 14·91, and 15·55 per cent. The theoretical composition is: Boron 84·62 per cent, carbon 15·38 per cent.—*Comptes Rendus.*

QUANTITATIVE SEPARATIONS OF METALS IN ALKALINE SOLUTIONS BY HYDROGEN PEROXIDE.

SEPARATION OF BISMUTH FROM COPPER.

By P. JANNASCH and J. LESINSKY.

1. *Precipitation of Bismuth in the Cold.*

As a suitable initial substance we used the metals themselves in the purest condition. We dissolved about 0·3 of each in 5 c.c. of concentrated nitric acid in a large porcelain capsule fitted with a handle, diluted the solution with 50 c.c. of water, and precipitated the bismuth with a mixture of 50 c.c. of 3 per cent hydrogen peroxide and 15 c.c. concentrated ammonia. The precipitating mixture is allowed to flow in a slow current with constant stirring, in order to avoid possible losses from the effervescence of the liquid. The faintly yellow amorphously-granular precipitate of bismuth hydro-peroxide thus obtained quickly subsides to the bottom of the liquid. The precipitate thus obtained is allowed to subside for a few minutes, and before filtration it is diluted with 100 c.c. water, in order to diminish the excessive action of the reagents upon the filter-paper. The paper, after transference to the filter, is washed first with a mixture of 2 vols. hydrogen peroxide, 1 vol. concentrated ammonia, and 8 vols. water, then with warm dilute ammonia (1 : 8), and lastly with plain hot water until the washings leave no residue if evaporated on sheet platinum.

In order to obtain accurate results, and especially to procure the bismuth as free as possible from copper at the first precipitation, the washing must be effected continuously and with the utmost care. Attention must be especially given to the point that even the parts of the filter not in contact with the precipitate and especially the edges of the filter are repeatedly extracted. In order to judge of the result, the funnel must be occasionally held up to the light, in order to recognise the presence of any blue reflection. The stream of water used must not be too powerful, as otherwise the paper is easily damaged, and thus minute particles of the precipitate are carried through mechanically. After the washing is completed, the precipitate is dried in the air-bath at 90—95°, placed along with the filter in a platinum crucible, and the incineration and ignition are effected exactly as directed in *Berichte* (xxvi., 1497).

The residue of bismuth oxides obtained in the crucible is first taken up in the smallest quantity of rather concentrated nitric acid, and the solution evaporated to dryness on the water-bath. The dry residue is then heated in a covered nickel beaker, raising the temperature gradually, and finally igniting with a free flame until all the nitric acid is expelled. The nitrate as it is being formed can only be prevented in this manner from spitting. Lastly, the residual bismuth oxide is fused and ignited until the weight becomes constant.

If commercial preparations of hydrogen peroxide are used, the results are in the first place too high, since on the precipitation with ammonia its impurities, such as silica and barium salt, are carried down at the same time.

The impurities of silica cannot be derived from the use of vessels of Berlin porcelain, since several special precipitations of bismuth (in presence of copper) executed in capacious platinum vessels gave exactly the same excess. Hence it is necessary to re-dissolve in nitric acid the bismuth oxide, after being weighed, to bring the insoluble particles carefully upon a small filter, to wash with very dilute hot nitric acid, to determine them separately, and to deduct them from the weight first obtained. These impurities amounted on an average to 0·0010—0·0025 grm., which in a total of 0·3 grm. taken for analysis makes a considerable excess, but if calculated on a total of 1 grm. in technical determinations is of less consequence.

The filtrate from the bismuth, holding all the copper in solution, is first evaporated in a Berlin porcelain capsule to expel the excess of ammonia, 15 c.c. of concentrated sulphuric acid are added, and the mixture is heated until all the nitric acid is completely expelled. It is then diluted, filtered off into a large beaker, the liquid is made up to at least 350 c.c. and the copper is precipitated as sulphide by prolonged heating with sulphuretted hydrogen. The gas is introduced until the precipitate, of a pure black colour, deposits rapidly at the bottom of the glass. The sulphide thus deposited filters quickly, and when washed with hot w .ter containing some sulphuretted hydrogen it never passes through turbid. Care must be taken, however, not to spirt the water on too strongly, which may easily occasion such a troublesome behaviour of the precipitate. An especial protection against turbid filtration is a skilfully directed application of the washing water from a small beaker provided with a spout. The washed copper sulphide is first dried in an air closet, and it is then incinerated along with the filter-paper (at first slowly) in a capacious porcelain crucible. The ash is then sufficiently crushed with a thick glass rod, and is finally ignited in a current of oxygen until the weight becomes constant. If a good blast-flame is finally used for ignition, there remains a faultlessly pure copper oxide, free from metallic copper and from traces of sulphuric acid. If the mass frits together strongly the operation of comminution is repeated after once treatment with oxygen. As very effective for a complete removal of sulphuric acid at the common temperatures of ignition obtained with ordinary burners, we have found the formerly-mentioned treatment of the copper oxide, or its moistening with ammonium carbonate, followed by evaporation and repeated ignition.

2. *Precipitation of Bismuth with the simultaneous Application of Heat.*

After the successful quantitative precipitation of bismuth by means of hydrogen peroxide in the cold, we attempted further to accelerate and simplify the operation of filtering by subsequently heating the pale yellow precipitate. In connection with these special experiments, the simultaneous action of hydroxylamine was studied.

(*a*) *Heating the Hydrated Bismuth Peroxide without the Presence of Hydroxylamine.*

0·3 grm. metallic bismuth and 0·3 grm. copper were dissolved in 5 c.c. concentrated nitric acid in a large Berlin capsule, diluted with 100 c.c. water and mixed in the cold, first with a mixture of 40 to 50 c.c. hydrogen peroxide and 15 c.c. concentrated ammonia. The whole was then heated for five to ten minutes on a boiling water-bath, 5 c.c. of boiling water are then added, and the whole is filtered at once. The pale yellow granular precipitate is at once washed with a mixture of 2 vols. hydrogen peroxide and 1 vol. concentrated ammonia, to which immediately before use there have been added 8 volumes of hot water; hot water alone is finally used. The precautions to be used in washing are the same as those to be observed in the precipitation of bismuth in the cold.

In the single accurate determinations which we undertook for the presence of copper in the quantities of bismuth oxide examined, not the slightest reaction was obtained with ammonium sulphide. To this end, the oxide in question was treated with nitric or hydrochloric acid, in which it dissolves without colouration, and it was again precipitated from this solution by a large excess of ammonia. The ammoniacal filtrate, which showed no blue tint, gave no precipitate with ammonium sulphide, nor even the slightest brown colour. (If much iron was present, faint green tints sometimes appeared, due to traces of ferrous sulphide). But on acidulation with acetic acid a faint copper reaction was produced by potassium ferrocyanide. These traces of copper thus detected in the weighed bismuth oxide are so slight as not to appreciably interfere with the quantitative result, so that for many determinations a single precipitation of the bismuth is suf-

ficient for its separation from copper. But if absolutely exact determinations are required a repeated solution and separation of the bismuth leads with certainty to the desired result.* In the second precipitation we were unable to detect the slightest traces of copper even with the very sensitive ferrocyanide reaction. In the filtrate from the repeated precipitate of bismuth we have on three occasions determined quantitatively the traces of copper present (a very troublesome operation) and found an average result of 0·00075 grm. on 0·3 grm. of copper taken.

(b) Precipitation of Bismuth in the simultaneous Presence of Hydroxylamine.

In presence of from 2 to 3 grms. hydroxylamine chloride, the granular amorphous yellow hydrated bismuth peroxide (as precipitated in the cold) takes a white colour and a crystalline texture (microscopic needles), which in the first precipitation obstinately retain traces of copper, but can be perfectly removed by a second precipitation. The hydroxylamine precipitate is still more easy to filter than the precipitate (*a*).

In comparison with the separation of bismuth from copper, either by precipitating the former with an excess of ammonia or by an excess of ammonium carbonate, our methods of precipitation above described deserve the decided preference. A mere precipitation with ammonia may be repeated three or four times without the bismuth being obtained perfectly free from copper. Similar, though not quite so bad, relations attend the separation with ammonium carbonate at ebullition, where, further, the determinations of bismuth generally come out too low, as bismuth carbonate is somewhat soluble in the excess of ammonium salts. Concerning the trustworthiness of the precipitation of bismuth with a large excess of water containing ammonium nitrate, we wish to reach a definite decision by certain special experiments.—*Berichte der Deutsch. Chem. Gesellschaft*, xviii., 2908.

THE QUESTION OF THE OCCURRENCE OF HYDROGEN PEROXIDE IN ATMOSPHERIC AIR AND IN ATMOSPHERIC WATERS.†

By EM. SCHÖNE.

(Continued from p. 174).

V. The experiment by which Iloswa believes that he has definitely proved the non-existence of ozone and hydrogen peroxide in the air, and which he has twice repeated without any essential modification, is as follows:—

Through an apparatus composed of eleven tubes containing in part reagents for the absorption and the detection of the substances in question, and in part agents for purification, air taken from a street of the city of Buda-Pesth was slowly drawn. Its volume was determined by a gas-meter. On the first occasion only 171¼ litres (about 8 c.c. per minute) passed through the apparatus in fifteen days, from April 25th to May 10th.

In the second experiment 500 litres (about 9½ c.c. per minute) were passed through in thirty-six days, from May 15th to June 20th.

It must in the first place strike us that the specimen experimented upon was the air of the streets of a great city which in 1886 had about 439,000 inhabitants, and in 1892 about 492,000. To deduce from two single experiments, carried out with such air, conclusions as to what is present or absent in normal air, is quite inadmissible.

The air entered directly a tube containing 20 c.c. soda-lye with the object of absorbing the hydrogen peroxide along with the main quantity of the nitrous and nitric acids. It was assumed that the former in the alkaline solution must oxidise the nitrous acid, and that if the former was present in excess it could be recognised by means of titanic acid after the completion of the experiment.

Naturally, this test gave a negative result, and Iloswa concludes that no hydrogen peroxide is present in atmospheric air.

But in an experiment arranged as above it was absolutely impossible to obtain reactions for peroxide, from the following grounds:—

1. Even if pure country air had been taken instead of street air, the volume used was too trifling to obtain recognisable quantities of peroxide in 20 c.c. of the absorptive liquid. In my experiments, performed in the years 1874 and 1875, at the season most favourable for the presence of hydrogen peroxide in country air (June 27th to July 15th) and in the most favourable meteorological conditions (fine weather), I obtained as the mean of determinations (conducted by day and night without interruption) only 0·38 c.c., = 0·0005776 grm. peroxide vapour in 1000 cubic metres; whence it may be calculated that in 500 litres of air there would be present the absolute quantity of 0·0000002888 grm. of hydrogen peroxide.

If we assume that in spite of the less favourable conditions under which Iloswa was experimenting, this absolute quantity of peroxide was present in the 500 litres of the street air of Buda-Pesth, that it had been condensed without loss in the 20 c.c. of soda-lye, and had remained undecomposed for five weeks, there would be obtained a solution of peroxide containing in one hundred million parts about 1½ parts of hydrogen peroxide—a proportion which cannot be detected with certainty by the most sensitive reaction.

2. It is well known that in alkaline liquids hydrogen peroxide, as well as the peroxides of the alkaline metals thence arising, are rather rapidly decomposed; on which subject Iloswa might have obtained more particular information if he had bestowed notice on the author's treatise on the behaviour of hydrogen peroxide with alkalis (*Ann. der Chemie*, cxciii., 241, 1878). How could he expect that in such a liquid the peroxide would prove permanent for five weeks, even if its quantity had been a thousand times greater than that obtained in his experiments?

3. That Iloswa could detect no hydrogen peroxide in the soda-lye proves merely, on his own supposition, that it, after effecting the possible oxidation of the nitrite into nitrate, was no longer present "in excess," but by no means that it was absent in the original air. As this soda-lye gives only a very feeble reaction with the extremely sensitive reaction of Griess, but a "more intense" reaction for nitrate with diphenylamine (relatively less sensitive), we must conclude that an oxidising agent of the atmosphere must here have been active, and as, according to Iloswa, ozone effects this oxidation less energetically than hydrogen peroxide, he might have regarded this oxidation as evidence that the latter (hydrogen peroxide) was really present in the air though not in excess.

As for ozone, the absence of which in the atmosphere is supposed to have been proved by this reaction, Iloswa used for the examination of the air several reagents:—(1) A dilute rose-coloured solution of the azobenzolnaphthylamine produced during Griess's reaction, which, as he observes, is turned yellow by ozone; (2) an acidulated solution of potassium iodide; (3) thallium paper; and (4) Wurster's tetramethyl paper. The first of these reagents was placed in the fifth tube of the apparatus, the potassium iodide solution in the seventh, and the two papers in the eighth. Before the air arrived at the first reagent, the azo-colouring matter, it passed through four tubes;

* The hydrated bismuth peroxide, whilst still moist, is placed along with the filter in a small beaker, and covered with about 25 c.c. of water; the whole being broken up by means of a glass rod, dissolved in 5 c.c. concentrated nitric acid with the aid of heat, filtered at once, and the filter at once washed with hot dilute nitric acid (1 : 10). The bismuth is again precipitated in the solution as above directed.

† *Berichte der Deutschen Chemischen Gesellschaft*, xxvi., p. 3011.

three of which contained soda lye and one dilute sulphuric acid, for the purpose of eliminating from the hydrogen peroxide nitrous acid, nitric acid, and ammonia.

Here Iloswa has quite overlooked the fact that the proportion of ozone in a gas is considerably reduced by passing even through empty tubes, still more through water, and very much more through alkaline lye. Any small quantity of ozone which under the most favourable circumstances might occur in normal air must have been completely destroyed in the first four tubes of the apparatus. It is therefore no wonder that his first reagent, the azo-colouring matter, gave no result.

Moreover Iloswa asserts that no reagent indicates the small quantities of ozone which are barely perceptible by smell. But as this smell cannot be recognised in the streets of Buda-Pesth, we must ask how under these conditions he could expect any indications from his reagents? Why, indeed, was this experiment requisite, as, according to his own statements, it could not indicate any ozone?

I do not understand, further, why the potassium iodide solution, introduced into the apparatus for the detection of ozone, was acidulated, since it is known that from the hydriodic acid thus liberated iodine is set free even by ordinary inactive oxygen, which in fact takes place. Thereby Iloswa has deprived his reagent of the power of giving evidence either for or against ozone; and not it alone, but the subsequent reagents thallium paper and "tetramethyl" paper, which must have been coloured by the iodine liberated from the acidulated solution of potassium iodide, and which were in fact coloured. Wherefore then the acidulation?

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1894.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, April 9th, 1894.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined two were recorded as "slightly turbid," and three as "clear, but dull." The remainder were clear, bright, and well filtered.

Four out of these five samples were from the East London mains at Cambridge Road, and their deviation from the usual brightness was due to the disturbance caused by the laying of 4200 yards of new 24-inch main and its connection with Cambridge Road and neighbourhood. The slight turbidity consisted chiefly of oxide of iron—a perfectly harmless body.

The rainfall during the month of March has been of a somewhat peculiar character. The mean quantity for this month over a period of twenty-five years is 1·59 inch, and the actual amount of rain recorded at Oxford has been 1·67 inch, showing an excess of 0·08 inch. But nearly the whole of this rain fell during the first half of the month, no less than 1·29 inch falling in three days, the 1st, the 12th, and the 14th. During the second half of the month, from the 15th to the 29th inclusive, not a drop of rain fell, and on the last two days only 4-100ths were recorded. As far, therefore as regards the filling of the springs and underground storage strata, the month just past may be considered a dry one, inasmuch as the bulk of the very heavy rain of the three wet days would have little opportunity of soaking into the ground, but would be hurried away along the water-courses to the sea. Taking the three months forming the first quarter of 1894, and comparing them with the corresponding quarter of 1893, we find that whereas in 1893 there was a deficiency of 1·07 inch, in 1894 there has been a deficiency of 0·76 inch.

In chemical composition the Thames-derived waters are rapidly approaching their high summer standard. The following Table shows that in every instance the good quality we remarked in our report for February has been slightly exceeded in March.

Averages of the Five Supplies Derived from the River Thames.

	Common salt per gallon.	Nitric acid per gallon.	Hardness, degrees.	Oxygen required per gallon.	Organic carbon per gallon.	Organic carbon per gallon.	Colour. Brown. Blue.
	Means.	Means.	Means.	Means.	Means.	Maxima.	Means.
Feb.	2·355	1·160	15·58	0·058	0·140	0·202	23·3 : 20
Mar.	2·285	1·101	15·32	0·052	0·121	0·162	21·3 : 20

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.

THE PRODUCTION OF CYANIDES.

By H. N. WARREN, Research Analyst.

SINCE the establishment of the cyanide process for the separation of gold from its ores, the synthetical race for the production of that compound, in quantity and at cheap rates, has been almost as keen as was the previous combat to reduce the alluvial deposits, and thus place upon the market the aluminium of to-day. Potassium nitrate, KNO_3, has long been experimented with in the hopes of replacing the oxygen equivalent by carbon, and by so doing produce KCN; but the large percentage of oxygen which is in every case set free at once determines the destruction of any cyanides thus formed, although traces of cyanides are always observed to be present after the partial reduction of commercial nitrates by means of carbon, owing to the secondary action of the ammonia thus formed, due to the moisture present.

Rochelle salt, mixed with a quarter of its weight of potassium nitrite, KNO_2, and ignited, has given 5 per cent as the highest yield of cyanide obtainable; while most hydrated carbonaceous substances yield a still lower per cent.

Anhydrous sodium acetate, in admixture with a nitrite, has yielded as much as 30 per cent of alkaline cyanide; whilst in a more recent experiment a mixture of 4 parts of wheaten flour to one of nitrate, and the whole thoroughly mixed with three of magnesia and compressed into blocks, yielded, after ignition, from a varying percentage up to 15 per cent of cyanide.

The production of sulphocyanides and reduction of the same by means of lime and carbon have on several occasions given valuable results in accordance with the following equation :—

$$KCNS + CaO + C = KCN + CaS + CO;$$

but at other times, in consequence, probably, of the difficulty in regulating the temperature, has resulted in the formation of worthless substitutes.

On returning to the old method for the production of cyanides, by the incineration of nitrogen compounds, a valuable addition will be found in the use of lime or barium oxide; probably both the barium and calcium cyanides are more readily formed than alkaline cyanides, and on lixiviation in contact with the alkaline carbonates present, they at once form alkaline cyanides and earthy carbonates or ferrocyanide, as arranged for. Again, potassium and sodium cyanide together are much easier to produce than either separate, fusing at a much lower temperature, and containing more cyanogen, in consequence of the difference in the equivalent of sodium when compared with potassium. A mixture of equal weights of the two alkalis reacts well in every respect, and yields good results.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

THE DETERMINATION OF NITROGEN.*

The Absolute or Cupric Oxide Method.

(Applicable to all Nitrogen Determinations).

The apparatus and reagents needed are as follows :—

Apparatus.

Combustion tube of best hard Bohemian glass, about 66 c.m. long and 12·7 m.m. internal diameter.

Azotometer of at least 100 c.c. capacity, accurately calibrated.

Sprengel mercury air-pump.

Small paper scoop, easily made from stiff writing paper.

Reagents.

Coarse Cupric Oxide or Wire Form.—To be ignited and cooled before using.

Fine Cupric Oxide.—Prepared by pounding ordinary cupric oxide in a mortar.

Metallic Copper.—Granulated copper, or fine copper gauze, reduced and cooled in a current of hydrogen.

Sodium Bicarbonate.—Free from organic matter.

Caustic Potash Solution.—Make a supersaturated solution of caustic potash in hot water. When absorption of carbonic acid ceases to be prompt, the solution must be discarded.

Manipulation.

Filling the Tube.—Of ordinary commercial fertilisers take 1 to 2 grms. for analysis. In the case of highly nitrogenised substances the amount to be taken must be regulated by the amount of nitrogen estimated to be present. Fill the tube as follows :—(1) About 5 c.m. of coarse cupric oxide. (2) Place on the small paper scoop enough of the fine cupric oxide to fill, after having been mixed with the substance to be analysed, about 10 c.m. of the tube; pour on this the substance, rinsing the watch-glass with a little of the fine oxide, and mix thoroughly with a spatula; pour into the tube, rinsing the scoop with a little fine oxide. (3) About 30 c.m. of coarse cupric oxide. (4) About 7 c.m. of metallic copper. (5) About 6 c.m. of coarse cupric oxide (anterior layer). (6) A small plug of asbestos. (7) 0·8 to 1 grm. of sodium bicarbonate. (8) A large loose plug of asbestos; place the tube in the furnace, leaving about 2·5 c.m. of it projecting; connect with the pump by a rubber stopper smeared with glycerol, taking care to make the connection perfectly tight.

Operation.

Exhaust the air from the tube by means of the pump. When a vacuum has been obtained allow the flow of mercury to continue; light the gas under that part of the tube containing the metallic copper, the anterior layer of cupric oxide (see 5th above), and the sodium bicarbonate. As soon as the vacuum is destroyed and the apparatus filled with carbonic acid, shut off the flow of mercury and at once introduce the delivery-tube of the pump into the receiving arm of the azotometer just below the surface of the mercury seal, so that the escaping bubbles will pass into the air and not into the tube, thus avoiding the useless saturation of the caustic potash solution.

When the flow of carbonic acid has very nearly or completely ceased, pass the delivery tube down into the receiving arm, so that the bubbles will escape into the azotometer. Light the gas under the 30 c.m. layer of oxide, heat gently for a few moments to drive out any moisture that may be present, and bring to red heat. Heat gradually the mixture of substance and oxide, lighting one jet at a time. Avoid a too rapid evolution of bubbles, which should be allowed to escape at the rate of about one per second or a little faster.

When the jets under the mixture have all been turned on, light the gas under the layer of oxide at the end of the tube. When the evolution of gas has ceased, turn out all the lights except those under the metallic copper and anterior layer of oxide, and allow to cool for a few moments. Exhaust with the pump and remove the azotometer before the flow of mercury is stopped. Break the connection of the tube with the pump, stop the flow of mercury, and extinguish the lights. Allow the azotometer to stand for at least an hour, or cool with a stream of water until a permanent volume and a temperature have been reached.

Adjust accurately the level of the KOH solution in bulb to that in the azotometer; note the volume of gas, temperature, and height of barometer; make calculation as usual, or read results from tables.

The Kjeldahl Method.

(Not applicable in presence of nitrates).

Reagents.

1. *Acid.*—(*a*) Standard hydrochloric acid, the absolute strength of which has been determined by precipitating with silver nitrate and weighing the silver chloride as follows :—

To any convenient quantity of the acid to be standardised: Add solution of silver nitrate in slight excess, and 2 c.c. pure nitric acid, specific gravity 1·2. Heat to boiling point and keep at this temperature for some minutes without allowing violent ebullition, and with constant stirring, until the precipitate assumes the granular form. Allow to cool somewhat, and then pass the fluid through the asbestos. Wash the precipitate by decantation, with 200 c.c. of very hot water, to which has been added 8 c.c. nitric acid and 2 c.c. dilute solution of silver nitrate containing 1 grm. of the salt in 100 c.c. of water. The washing by decantation is performed by adding the hot mixture in small quantities at a time, and beating up the precipitate well with a thin glass rod after each addition. The pump is kept in action all the time, but to keep out dust during the washing the cover is only removed from the crucible when the fluid is to be added.

Put the capsule and precipitate aside, return the washings once through the asbestos so as to obtain them quite clear, remove them from the filter, and set aside to recover excess of silver. Rinse the receiver, and complete the washing of the precipitate with about 200 c.c. of cold water. Half of this is used to wash by decantation and

* Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (American) at its Meeting at Chicago, August, 1893.

the remainder to transfer the precipitate to the crucible with the aid of a trimmed feather. Finish washing in the crucible, the lumps of silver chloride being broken down with the glass rod. Remove the second filtrate from the receiver and pass about 20 c.c. of 98 per cent alcohol through the precipitate. Dry at 140° to 150°. Exposure for half an hour is found more than sufficient, at this temperature, to dry the precipitate thoroughly.

Or (*b*) standard sulphuric acid, the absolute strength of which has been determined by precipitation with barium chloride, and weighing the resulting barium sulphate.

For ordinary work, half normal acid is recommended; *i.e.*, acid containing 18·2285 grms. of hydrochloric acid or 24·5185 grms. sulphuric acid to the litre; for work in determining very small amounts of nitrogen, one-tenth normal acid is recommended. In titrating mineral acids against ammonia solutions, use cochineal as indicator.

2. *Standard ammonia*, the strength of which, relative to the acid, has been accurately determined. One-tenth normal ammonia solution, *i.e.*, containing 1·7051 grms. of ammonia to the litre, is recommended for accurate work.

3. *Sulphuric acid*, specific gravity 1·84, free from nitrates and also from ammonium sulphate, which is sometimes added in the process of manufacture to destroy oxides of nitrogen.

4. *Metallic mercury*, or mercuric oxide, prepared in the wet way. That prepared from mercuric nitrate cannot be safely used.

5. *Potassium permanganate* finely pulverised.

6. *Granulated zinc*, pumice stone, or 0·5 grm. of zinc dust are to be added to the contents of the flasks in distillation, when found necessary, in order to prevent bumping.

7. *Potassium Sulphide.*—A solution of 40 grms. of commercial potassium sulphide in 1 litre of water.

8. *Soda.*—A saturated solution of sodium hydrate free from nitrates.

9. *Indicator.*—Solution of cochineal prepared as follows:—Tincture of cochineal is prepared by digesting and frequently agitating 3 grms. of pulverised cochineal in a mixture of 50 c.c. of strong alcohol with 200 c.c. of distilled water, at ordinary temperatures, for a day or two. The solution is decanted or filtered through Swedish paper.

Apparatus.

1. *Kjeldahl digestion flasks* of hard, moderately thick, well-annealed glass. These flasks are about 22 c.m. long, with a round pear-shaped bottom, having a maximum diameter of 6 c.m., and tapering out gradually in a long neck, which is 2 c.m. in diameter at the narrowest part, and flared a little at the edge. The total capacity is 225 to 250 c.c.

2. *Distillation flasks* of ordinary shape, of 550 c.c. capacity, or preferably flasks of the same capacity, of pear-shaped bottom, of well-annealed glass, for both digestion and distillation, fitted with a rubber stopper and a bulb-tube above to prevent the possibility of sodium hydrate being carried over mechanically during distillation. The bulbs are about 3 c.m. in diameter, the tubes being of the same diameter as the condenser and cut off obliquely at the lower end. This is adjusted to the tube of the condenser by a rubber tube.

Manipulation.

1. *The Digestion.*—0·7 to 0·8 grm. of the substance to be analysed, according to its proportion of nitrogen, is brought into a digestion flask with approximately 0·7 grm. of mercuric oxide or its equivalent in metallic mercury and 22 c.c. of sulphuric acid. The flask is placed in an inclined position, and heated below the boiling-point of the acid for from five or fifteen minutes, or until frothing has ceased. If the mixture froths badly, a small piece of paraffin may be addded to prevent it. The heat is then raised until the acid boils briskly. No further attention is required till the contents of the flask have become a clear liquid, which is colourless or at least has only a very pale straw colour. The flask is then removed from the frame, held upright, and, while still hot, potassium permanganate is dropped in carefully and in small quantities at a time till, after shaking, the liquid remains of a green or purple colour.

2. *The Distillation.*—After cooling, the contents of the flask are transferred to the distilling flask with about 200 c.c. of water, with a few pieces of granulated zinc, pumice stone, or 0·5 grm. of zinc dust when found necessary to keep the contents of the flask from bumping, and 25 c.c. of potassium sulphide solution are added, shaking the flask to mix its contents. Next add 50 c.c. of the soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the sides of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 c.c. of the distillate will generally contain all the ammonia. This operation usually requires from forty minutes to one hour and a half. The distillate is then titrated with standard ammonia.

The use of mercuric oxide in this operation greatly shortens the time necessary for digestion, which is rarely over an hour and a half in case of substances most difficult to oxidise, and is more commonly less than an hour. In most cases the use of potassium permanganate is quite unnecessary, but it is believed that in exceptional cases it is required for complete oxidation, and in view of the uncertainty it is always used. The potassium sulphide removes all the mercury from the solution, and so prevents the formation of mercur-ammonium compounds which are not completely decomposed by soda solution. The addition of zinc gives rise to an evolution of hydrogen and prevents violent bumping. Previous to use the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates that are present, which might otherwise escape notice.

Gunning Method.

Manipulation.

In a digestion flask holding from 250 to 500 c.c. place from 0·7 to 2·8 grms. of the substance to be analysed, according to its proportion of nitrogen. Then add 10 grms. of powdered potassium sulphate and from 15 to 25 c.c. (ordinarily about 20 c.c.) of concentrated sulphuric acid. Conduct the digestion as in the Kjeldahl process, starting with a temperature below boiling-point and increasing the heat gradually until frothing ceases. Digest until colourless or nearly so. (Do not add either potassium permanganate or potassium sulphide). Dilute, neutralise, and distil as in the Kjeldahl method. In neutralising, it is convenient to add a few drops of phenolphthalein indicator, by which one can tell when the acid is completely neutralised, remembering that the pink colour, which indicates an alkaline reaction, is destroyed by a considerable excess of strong fixed alkali. The distillation and titration are conducted as in the Kjeldahl method.

Kjeldahl Method Modified to Include the Nitrogen of Nitrates.

(Applicable to all Fertilisers containing Nitrates).

Besides the reagents and apparatus given under the Kjeldahl method, there will be needed:—

1. *Zinc Dust.*—This should be an impalpable powder; granulated zinc or zinc filings will not answer.

2. *Sodium thiosulphate.*

3. *Commercial salicylic acid.*

The Determination.

Bring from 0·7 to 1·4 grms. of the substance to be analysed into a Kjeldahl digesting flask, add to this 30 c.c. of sulphuric acid containing 1 grm. of salicylic acid, and shake thoroughly; then add 5 grms. of crystallised sodium

thiosulphate, or add to the substance 30 c.c. of sulphuric acid containing 2 grms. of salicylic acid; then add gradually 2 grms. of zinc dust, shaking the contents of the flask at the same time. Finally place the flask on the stand for holding the digestion flasks, where it is heated over a low flame until all danger from frothing has passed. The heat is then raised until the acid boils briskly, and the boiling continued until white fumes no longer pour out of the flask. This requires about five or ten minutes. Add now approximately 0·7 grm. of mercuric oxide or its equivalent in metallic mercury, and continue the boiling until the liquid in the flask is colourless or nearly so. (In case the contents of the flask are likely to become solid before this point is reached, add 10 c.c. more of sulphuric acid). Complete the oxidation with a little potassium permanganate in the usual way and proceed with the distillation as described in the Kjeldahl method. The reagents should be tested by blank experiments.

Gunning Method Modified to Include the Nitrogen of Nitrates.

Manipulation.

In a digestion flask holding from 250 to 500 c.c. place from 0·7 to 2·8 grms. of the substance to be analysed, according to the amount of nitrogen present. Ten grms. of potassium sulphate, 5 grms. of sodium thiosulphate, and 30—35 c.c. of the salicylic acid mixture, *i.e.*, 30 c.c. sulphuric acid, to 1 grm. of salicylic acid, are then added, and the whole digested at a low temperature until frothing ceases. Then heat strongly until the solution becomes colourless or nearly so. Dilute, neutralise, and distil, as in the Gunning method.

Alternate Methods.

Ruffle Method.

Reagents.

1. Standard solutions and indicator the same as for the Kjeldahl method.
2. A mixture of equal parts by weight of fine slaked lime and finely powdered sodium thiosulphate dried at 100°.
3. A mixture of equal parts by weight of finely powdered granulated sugar and flowers of sulphur.
4. Granulated soda-lime, as described under the Soda-lime Method.

Apparatus.

5. Combustion tubes of hard Bohemian glass, 30 c.m. long and 1·3 c.m. in diameter.
6. Bulbed U-tubes or Will's bulbs, as described under the Soda-lime Method.

Manipulations.

1. Clean the U-tube and introduce 10 c.c. of standard acid.
2. Fit the cork and glass connecting tube. Fill the tube as follows:—(1) A loosely fitting plug of asbestos, previously ignited, and then 2·5 to 3·5 c.m. of the thiosulphate mixture. (2) The weighed portion of the substance to be analysed is intimately mixed with from 5 to 10 grms. of the sugar and sulphur mixture. (3) Pour on a piece of glazed paper or in a porcelain mortar a sufficient quantity of thiosulphate mixture to fill about 25 c.m. of tube; then add the substance to be analysed, as previously prepared, mix carefully, and pour into the tube; shake down the contents of the tube; rinse off the paper or mortar with a small quantity of the thiosulphate mixture and pour into the tube; then fill up with soda-lime to within 5 c.m. of the end of the tube. (4) Place another plug of ignited asbestos at the end of the tube and close with a cork. (5) Hold the tube in a horizontal position and tap on the table until there is a gas channel all along the top of the tube. Make connections with the U-tube containing the acid; aspirate, and see that the apparatus is tight.

The Combustion.—Place the prepared combustion tube in the furnace, letting the open end project a little, so as not to burn the cork. Commence by heating the soda-lime portion until it is brought to a full red heat. Then turn on slowly jet after jet towards the outer end of the tube, so that the bubbles come off two or three a second. When the whole tube is red hot, and the evolution of the gas has ceased, and the liquid in the U-tube begins to recede towards the furnace, attach the aspirator to the other limb of the U-tube, break off the end of the tube, and draw a current of air through for a few minutes. Detach the U-tube and wash the contents into a beaker or porcelain dish; add a few drops of the cochineal solution, and titrate.

Soda-lime Method.

(Not Applicable in presence of Nitrates).

Reagents and Apparatus.

1. Standard solutions and indicator the same as for the Kjeldahl method.
2. Granulated soda-lime, fine enough to pass a 2·5 m.m. sieve and thoroughly dry.
3. Fine soda-lime, fine enough to pass a 1·25 m.m. sieve, also thoroughly dry.

Excellent soda-lime may be easily and cheaply prepared by slaking 2¼ parts of quicklime with a strong solution of 1 part of commercial caustic soda (such soda as is used in the Kjeldahl process), care being taken that there is enough water in the solution to slake the lime. The mixture is then dried and heated in an iron pot to incipient fusion, and when cold ground and sifted as above.

Instead of soda-lime Johnson's mixture of carbonate of soda and lime or slaked lime may be used.

Slaked lime may be granulated by mixing it with a little water to form a thick mass, which is dried in the water-oven until hard and brittle. It is then ground and sifted as above. Slaked lime is much easier to work with than soda-lime, and gives excellent results, though it is probable that more of it should be used in proportion to the substance to be analysed than is the case with soda-lime.

4. Asbestos which has been ignited and kept in a glass-stoppered bottle.
5. Combustion tubes about 40 c.m. long and of 12 m.m. internal diameter, drawn out to a point and closed at one end.
6. Large-bulbed U-tubes with glass stopcock, or Will's tubes with four bulbs.

Manipulation.

The substance to be analysed should be powdered fine enough to pass through a sieve of 1 m.m. mesh; 0·7 to 1·4 grms., according to the amount of nitrogen present, is taken for the determination. Into the closed end of the combustion tube put a small loose plug of asbestos, and upon it about 4 c.m. of fine soda-lime. In a porcelain dish or mortar mix the substance to be analysed, thoroughly but quickly, with enough fine soda-lime to fill about 16 c.m. of the tube, or about forty times as much soda-lime as substance, and put the mixture into the combustion tube as quickly as possible by means of a wide necked funnel, rinsing out the dish and funnel with a little more fine soda-lime, which is to be put in on top of the mixture. Fill the rest of the tube to about 5 c.m. of the end with granulated soda-lime, making it as compact as possible by tapping the tube gently while held in a nearly upright position during the filling. The layer of granulated soda-lime should not be less than 12 c.m. long. Lastly, put in a plug of asbestos about 2 c.m. long, pressed rather tightly, and wipe out the end of the tube to free it from adhering soda-lime.

Connect the tube by means of a well-fitting rubber stopper or cork with the U-tube or Will's bulbs, containing 10 c.c. of standard acid, and adjust it in the combustion furnace so that the end projects about 4 c.m. from the furnace, supporting the U-tube or Will's bulb suitably

Heat the portion of the tube containing the granulated soda-lime to a moderate redness, and when this is attained extend the heat gradually through the portion containing the substance, so as to keep up a moderate and regular flow of gases through the bulbs, maintaining the heat of the first part until the whole tube is heated uniformly to the same degree. Keep up the heat until gases have ceased bubbling through the acid in the bulbs, and the mixture of substance and soda-lime has become white, or nearly so, which shows that the combustion is finished. The combustion should occupy about three-quarters of an hour or not more than one hour. Remove the heat, and when the tube has cooled below redness break off the closed tip and aspirate air slowly through the apparatus for two or three minutes to bring all the ammonia into the acid. Disconnect, wash the acid into a beaker or flask, and titrate with the standard alkali.

During the combustion the end of the tube projecting from the furnace must be kept heated sufficiently to prevent the condensation of moisture, yet not enough to char the stopper. The heat may be regulated by a shield of tin slipped over the projecting end of the combustion tube.

It is found very advantageous to attach a Bunsen valve to the exit tube, allowing the evolved gases to pass out freely, but preventing a violent "sucking back" in case of a sudden condensation of steam in the bulbs.

REPORT OF COMMITTEE ON DETERMINATIONS OF ATOMIC WEIGHT PUBLISHED DURING 1893.*

By F. W. CLARKE.

(Continued from p. 179).

Palladium.

Atomic weight determined by Joly and Leidié by means of potassium palladio-chloride, K_2PdCl_4 (*Comptes Rendus*, cxvi., 147, 1893; results calculated with O = 15·96, Cl = 35·37, KCl = 74·40, and H = 1). In the first series of experiments the salt was dried in vacuo at ordinary temperature. It was then electrolysed in a solution acidulated with hydrochloric acid, both the palladium and the potassium chloride being weighed. The palladium was dried, ignited in a stream of hydrogen, and cooled in an atmosphere of carbon dioxide. Results as follows:—

			At. wt. Pd.	
Wt. salt.	Wt. Pd.	Wt. KCl.	From salt : Pd.	Pd : 2KCl.
1·0255	0·3919	0·5520	105·749	105·643
1·2178	0·3937	0·5551	104·881	105·535
1·2518	0·4048	0·5687	104·923	105·916

This series was rejected by the authors upon finding that the salt retained water. In one experiment 0·23 per cent of water was found. Accordingly a second set of determinations was made in which the palladio-chloride was dried in vacuo at 100°.

			At. wt. Pd.	
Wt. salt.	Wt. Pd.	Wt. KCl.	Salt : Pd.	Pd : 2KCl.
1·3635	0·4422	0·6186	105·374	106·368
3·0628	0·9944	1·3929	105·545	106·229
1·4845	0·4816	0·6782	105·405	105·694
1·7995	0·5838	0·8206	105·427	105·861

The mean of the values found from the ratio K_2PdCl_4:Pd is 105·438. If O = 16, this becomes Pd = 105·702. With O = 15·88 we get 104·910. The KCl values were rejected.

Still another set of determinations was based upon the reduction of the double chloride in a steam of hydrogen, the data being in other respects like the foregoing. Results as follows:—

			At. wt. Pd.	
Wt. salt.	Wt. Pd.	Wt. KCl.	Salt : Pd.	Pd : KCl.
2·4481	0·7949	1·1168	105·560	105·911
1·8250	0·5930	0·8360	105·671	105·656

It is noticeable that these values, in the set K_2PdCl_4 : Pd, run higher than in the electrolytic series. Inasmuch as the latter experiments were made in presence of free hydrochloric acid, it would seem possible that chlorine may have been liberated, preventing complete precipitation of the palladium, and so slightly lowering the apparent atomic weight of the latter. At all events, the results obtained are not sharply concordant, and are, therefore, inconclusive.

Barium.

An elaborate memoir upon the atomic weight of barium, by Richards (*Proc. Amer. Acad.*, xxviii., 1; presented Jan. 11, 1893), makes a notable change in the value of that constant. Barium bromide was the compound investigated, and the procedure consisted in titrating its solution with solutions containing known quantities of silver. In many of the experiments the silver bromide thrown down during titration was collected and weighed. From the weights of Ag and of AgBr found, the ratio Ag : Br may be computed as a check on the accuracy of the work.

Full details are given concerning purity of materials, processes, weighings, &c., for which the original memoir must be consulted. The final results are stated in the following columns: First, $BaBr_2$ corresponding to 100 parts Ag. Second, $BaBr_2$ corresponding to 174·080 parts AgBr. Third, percentage of Ag in AgBr.

Expt.	I.	II.	III.
1	137·746	137·783	57·460
2	137·736	137·760	57·455
3	—	137·723	—
4	137·732	—	—
5	137·735	137·739	57·447
6	137·748	137·748	57·445
7	137·747	—	—
8	137·740	137·747	57·448
9	137·755	137·748	57·442
10	137·738	137·752	57·441
11	137·747	137·772	57·455
12	—	137·726	—
14	137·750	137·745	57·443
15	137·756	137·754	57·445
16	137·731	—	—
17	137·748	—	—
18	—	137·745	—
19	137·759	137·758	57·445
Mean, omitting 1 and 2 ..	137·745	137·747	57·448
		Stas found ..	57·445

The last column, by its agreement with Stas' measurements, serves to confirm the other two, from which the atomic weight of barium is easily computed. From the ratio $Ag_2 : BaBr_2$, when Ag = 107·93 and Br = 79·955, Ba = 137·426. From the ratio 2AgBr : $BaBr_2$, Ba = 137·431.

The value 137·43, then, must replace the lower value commonly held hitherto. The new results appear to be thoroughly established and unimpeachable.

(To be continued.)

Blue Colouration Assumed by Leuko-auramine in Contact with Acids.—A. Rosenstiehl.—Leuko-auramine does not exist in the form of a blue compound. The substance which Graebe considered as such is the tetramethylic-diamido-benzhydrol, the chlorhydrine of which has a rich blue colouration.—*Compt. Rend.*, cxviii., No. 14.

* From the *Journal of the American Chemical Society*, xvi., No. 3.

NOTICES OF BOOKS.

An Outline of Qualitative Analysis. By J. A. Miller, M.Sc., A.M., Ph.D. (Berlin), Professor of Medical Chemistry and Toxicology and Director of the Chemical Laboratory at the Medical Department of the Niagara University of Buffalo, N.Y.; Member of the Berlin Chemical Society; Fellow of the London Chemical Society; Member of the American Chemical Society and of the American Microscopical Society; Fellow of the Royal Microscopical Society. New York and London: The Scientific Publishing Co. 1894. 8vo, pp. 58.

We have here a compact and well arranged manual of inorganic qualitative analysis. The instructions given are, as we might expect, accurate in accordance with our present knowledge. The blowpipe reactions and, where desirable, the spectroscopic characters of the substances in question are indicated. But the rare elements and their compounds, even platinum and its associated metals, have been omitted, probably in order to economise space, since the author remarks in his preface that the time usually devoted to the study of general and practical chemistry "is so limited that the use of such large manuals as Fresenius, &c., is hardly admissible." This may be true, and if so "pity 'tis 'tis true."

In the table of elements glucinum bears its Continental name beryllium. Otherwise we meet with no terminology at which a British student will be surprised, except the abbreviation or contraction "urinalysis" for analysis of urine.

The only drawback to this otherwise valuable work is its subject. There is probably, in England at least, no department of science which has been so richly supplied with manuals and text-books as elementary chemistry. Had Professor Miller's work made its appearance a quarter of a century ago, we should have been able to speak of it with nearly unqualified approbation.

A Manual of Microchemical Analysis. By Professor H. Behrens, of the Polytechnic School of Delft, Holland. With an Introductory Chapter by Professor John W. Judd, F.R.S., of the Royal College of Science, London. With 84 Illustrations, drawn by the Author. London: Macmillan and Co. (and New York). 1894. Small 8vo, pp. 246.

Microchemical analysis is a subject which has not figured extensively—we might say not adequately—in English literature. We are therefore the more eager to welcome the thoroughly practical work of Prof. Behrens. The geologist, the mineralogist, the prospector, the superintendent of mines, or the metallurgist, if unversed in microchemical analysis, will often find himself at a loss.

The author does not exaggerate when he says that "by assiduous study microchemical analysis will be developed into a system that will rival blowpipe analysis as regards its rapidity and its unassuming character with regard to space and laboratory appliances, and in many instances surpass blowpipe analysis in the variety and delicacy of its tests." For the travelling *savant* microchemistry is indispensable.

In Part I. the author treats of microchemical apparatus, reagents, and reactions. He recommends the beginner to work through the reactions of the elements as here laid down.

In Part II. we find a systematic scheme for the examination of mixed compounds, both liquids and solids. There are directions for qualitative water analysis, arranged for samples of about 40 c.c. and dispensing with cumbrous appliances. By the methods here laid down, the water may be tested for potassium, sodium, calcium, magnesium, lead; for chlorides, phosphates, sulphates, and carbonates; for ammonia and nitrous acid.

Among possible causes of error in microchemical work, the author points out the impurity of distilled water,—silica and alkali, taken up on prolonged contact even with hard glass. For exact work the water must be distilled for the occasion. Heating and evaporating strong acids on glass slides is always to be looked upon as involving a source of error.

For ascertaining the reaction on solution, the author seems to prefer litmus or congo-red, the superior delicacy of the former being "in some cases more than counterbalanced by the impurities it always contains." The detection of traces of the precious metals is recommended to be done in the dry way.

Special directions are given for the examination of rocks in the state of slices or of powder, of alloys, and of combinations of rare elements, including the compounds of the cerite metals. From an examination of this work the reader must carry away the conviction that Professor Behrens is an exceedingly accurate and delicate worker, and that the student who follows his instructions will not be led astray.

It does not appear whether this work—excluding Prof. Judd's introductory chapter—has been translated from a Dutch original or whether it has been written in English by Prof. Behrens. From some peculiarities we should be apt to infer the latter. Thus we find "beryllium" written in place of glucinum, and fuchsine instead of magenta. Another peculiarity is that the author uses for "cubic centimetres" not the abridgment c.c., universally employed in England as well as in France, but a more prolix symbol.

The work well deserves to be strongly recommended.

Handbook of the Nitrogenous Ortho-condensation Products ("Handbuch der Stickstoffhaltigen Ortho-condensations producte"). By Dr. O. Kühling, Private Tutor at the Royal Technical High School of Berlin. Berlin: R. Oppenheim (Gustav Schmidt). 1893. 8vo, pp. 628.

A main object of this work is to afford a systematic view of a region which has only been elaborated periodically and piece-meal. On the other hand, it is calculated to save the chemical investigator the tedious labour of searching out what—if anything—has already been done in any given group.

Hence it is likely to be extremely useful alike to the scientific chemist engaged in research and to the manufacturer of the coal-tar colours.

The work comprises a general and a special part. The former discusses the constitution of the ortho-condensation products, presenting generalities on the synthesis of these products in as far as they are nitrogenous, and describes their properties, physical and chemical, as modified by substitutions, the properties of their hydroproducts, their reactions of decomposition and of transposition, and their technical applications, chiefly of a tinctorial character.

The special part gives an account—necessarily brief—of the compounds having respectively condensation rings of four, of five, of six, and of more than six members.

The value of Dr. Kühling's work is unquestionable.

How the Phylloxera May and Ought to be Prevented ("Come si Può e si Deve Prevenire La Fillossera"). By Prof. Adolfo Casali, Director of the Chemical Agricultural Laboratory of Bologna. Bologna: Zanichelli. 1893. Pp. 77.

As regard the war against the phylloxera, the author rightly maintains that prevention is better than repression. The phylloxera has been, not indeed created, but favoured in its ravages by the unhealthy, anæmic, or, as he terms it, jaundiced condition of the vines. For the repair or correction of the soils, he recommends the subjoined mixture:—

Pyrites, or artificial ferrous sulphide ..	40 parts.
Quicklime	15 ,,
Gypsum	10 ,,
Recent turf, tanniferous residues of skins, &c.	10 ,,
Oil cakes, of castor, colza, sesame, or other seeds	25 ,,
	100 ,,

This mixture is to be freely added to a soil, preferably sandy. He does not seem to lay any weight upon the addition of potash, a base which is largely taken up by the vine, and is returned to the soil only very sparingly. It is sad to consider what havoc has been occasioned in the eastern hemisphere by the ill-judged and utterly needless importation of American vines.

Prof. Casali's treatment is cheap and convenient in its application, and demands merely materials which are universally available.

OBITUARY.

Dr. A. HILL HASSALL.

The death is just announced of Dr. A. Hill Hassall. The deceased in early life turned his attention mainly to analytical chemistry, and about forty years ago he became widely known as the leading spirit of the *Lancet* Commission on the "Adulteration of Foods, Drinks, and Drugs." Of late years he has been comparatively little known, and seems, indeed, to have retired from the analytical profession.

CORRESPONDENCE.

SOLVENTS OF CELLULOSE.

To the Editor of the Chemical News.

Sir,—In the Chemical News, lxix., 174, you publish a notice of researches of Dr. Hanousek, in which we are made responsible for the proposal of a reagent consisting of "a solution of zinc chloride in two parts by weight of acetic anhydride" as a solvent for cellulose.

In case anyone should be misled by a confusion which will be obvious to most, we would point out that the *solvent* referred to is a solution of $ZnCl_2$ (one part) in 40 per cent HCl.Aq (two parts). Acetic anhydride in presence of $ZnCl_2$ dissolves and *acetylates* (Franchimont), but the salt is added only in minute quantity. A "solution of $ZnCl_2$ in $\overline{Ac}_2O$ (two parts)" would be an interesting problem in preparations!—We are, &c.,

C. F. Cross and E. J. Bevan.

Laboratory, 4, New Court,
Lincoln's Inn, London, W.C.,
April 13, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 14, April 2, 1894.

The death of the illustrious physiologist, Dr. Brown-Sequard, — which took place on the 1st inst., — was officially announced.

Action of Water on Calcium Biphosphate.—A. Joly and E. Sorel.—If thrown into boiling water the crystals of the hydrated salt are rapidly devitrified, and the liquid, acid to litmus, though neutral to methyl-orange, contains a mono-phosphate. If the deposit is isolated it appears on microscopic examination that every trace of crystallisation has disappeared, and that a tricalcium salt has been formed which may be obtained pure if the action of boiling water is repeated two or three times. If dried at the ordinary temperature over sulphuric acid, its composition is $(PO_4)_2Ca_3+\frac{1}{2}H_2O$. If the ebullition is maintained, the volume of the water remaining constant, a second reaction takes place between the liquid and the precipitate, when small crystals appear. If the weight of the bicalcium salt is less than 10 grs. per litre, the final product is $CaOP_2O_5$. The determination of the water in the alkaline-earthy phosphates presents difficulties to which the authors purpose returning on a future occasion.

Fixation of Iodine by Starch.—E. G. Rouvier.—When the proportion of iodine is comprised between 13 and 17·5 per cent, the quantity of iodine fixed is approximately proportional to the square root of the quantity of iodine added. Below 13 per cent the quantity of iodine increases more rapidly, but above 17·5 per cent it increases more slowly.

A Vegetable Malady Occasioned by Botrytis Cinerea.—Prillieux and Delacroix.—The plants attacked have their roots surrounded by a fine net-work of filaments, which form a real tissue. The leaves of the plant turn yellow, fade, blacken, and putrefy. It attacks a great number of plants in the open air, but it is most dangerous in conservatories. There are hopes of preventing it by means of cupric dressings, such as the Bordeaux broth employed against the mildew and the "black-rot" of vines.

Spark-spectra of Certain Minerals.—A. de Gramont.—In a former paper (March 12, 1894, p. 591) the author describes his method of experimentation, and he now extends his researches to other mineral species.

Oligiste, Fe_2O_3.—A bad conductor; no results.

Cuprite (Chili).—Some spectrum as native copper and chalcosine.

Cassiterite (Cornwall).—Gives distinctly the two rays of tin β (563) and α (452).

Anatase (Oisans).—Fine characteristic spectrum of titanium formed of a series of groups of very fine rays in echelon over the whole spectrum. The maxima are at (519), (504), (453), (430).

Rutile.—Gives nothing.

Ilmenite (Norway).—Gives, especially with hydrochloric acid, the chief rays of iron, but not that of titanium.

Franklinite (New Jersey).—When moistened with HCl gives with difficulty the rays of zinc.

Pechuranium, U_3O_4 (Bohemia).—This mineral contains generally lead (3 to 10 per cent), and gives the principal rays of this metal only.

Allemontite, $SbAs_3$ (Allemont).—Gives a fine spectrum, in which the rays of arsenic predominate.

Leucopyrite, $FeAs_2$.—A fine complete spectrum of iron with the rays of arsenic superimposed.

Nickeline, NiAs, (Thuringen).—A fine spectrum, with rays of arsenic and nickel.

Smaltine (Fe,Co)As_2, (Valais).—Rays of arsenic predominate. Those of iron more visible and distinct than those of cobalt.

Domeykite, Cu_2As, (Mexico).—A good spectrum of copper and arsenic and some rays of iron, especially Feα(527).

Mispickel, Fe(As,S), (Cantal).—The same spectrum as leukopyrite, the sulphur not seeming to interfere.

Cobaltine, Co(As,S), (Nassau).—The rays of cobalt are much more distinct than in smaltine, and have been measured. The rays of arsenic predominate and there are several rays of iron.

Discrase, Ag_3Sb.—Intense rays of silver and the chief rays of antimony.

The sulphantimonides under the action of the spark evolve copious fumes of antimony oxide which cover the forceps with a white coating. A characteristic reaction.

Psaturose, $5Ag_2S.Sb_2S_3$, (Freiberg), and *Pyargyrite*, $3Ag_2S.Sb_2S_3$, (Bohemia).—Both give the rays of antimony and the two rays of silver, α (546) and β (521).

Boulangerite, $3PbS.Sb_2S_3$, (Nassau), and *Jamesonite*, $2PbS,Sb_2S_3$, (Cornwall).—Besides the rays of antimony both give the principal rays of lead.

Zinckenite, $PbS.Sb_2S_3$, (Hartz).—Same spectrum of antimony and lead, besides the rays of arsenic.

Bournonite, $3(Pb,Cu_2)S,Sb_2.S_3$, (Hartz).—Weak rays of antimony; rays of lead and especially of copper intense.

Panabase, $4(CuSbS_2)+3Cu_2S+2ZnS)$, (Hartz).—Rays of antimony not visible, but those of copper and zinc intense. Some specimens give the violet rays of lead and the silver ray α (546).

Senarmontite, Sb_2O_3, (Constantine), gives fugitive rays of Sb.

The following, if moistened with a drop of dilute HCl, give more satisfactory results:—

Boleite, *Cumengeite*, *Crocoise* (a good spectrum of chrome), *Cerargyrite*, *Eulytite*, ray α of bismuth, *Anglesite*, α ray of lead.

Molybdenite, *Acerdese*, and *Wolfram* gave nothing.

MEETINGS FOR THE WEEK.

TUESDAY, 24th.—Royal Institution, 3. "Electric Illumination," by Prof. J. A. Fleming, F.R.S.
—— Institute of Civil Engineers, 8.
—— Medical and Chirurgical, 8.30.
—— Photographic, 8.
WEDNESDAY, 25th.—Society of Arts, 8. "Some Recent Developments of Photographic Chemistry," by Chapman Jones, F.C.S.
—— British Astronomical, 5.
—— Geological, 8.
THURSDAY, 26th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "Mozart as a Teacher" (with Musical Illustrations), by Prof. J. F. Bridge, Mus.Doc.
—— Institute of Electrical Engineers, 8.
—— Society of Arts, 4.30. "Municipal and Village Water Supply and Sanitation in the North-West Provinces and Oudh," by Sir Auckland Colvin, K.C.S.I.
FRIDAY, 27th.—Royal Institution, 9. "Action of Light on Bacteria and Fungi," by Prof. H. Marshall Ward F.R.S.
—— Physical, 5. "The Mechanism of Electrical Conduction," by Dr. C. V. Burton. "A Graphic Method of Constructing the Curves of Current in Electromagnets-Transformers," by Major Hippesley, R.E. "The Design and Winding of Alternate Current Electromagnets," by Prof. S. P. Thompson, F.R.S.
SATURDAY, 28th.—Royal Institution, 3. "Literature and Journalism,' by H. D. Traill, D.C.L.

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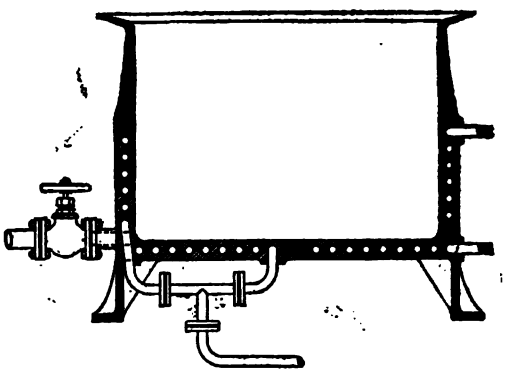

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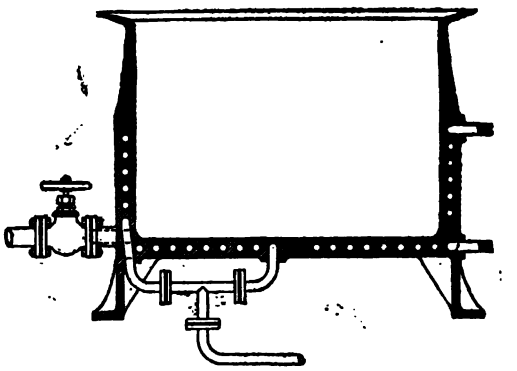

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says:—
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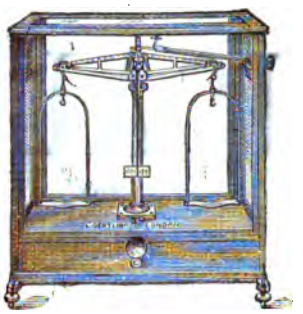

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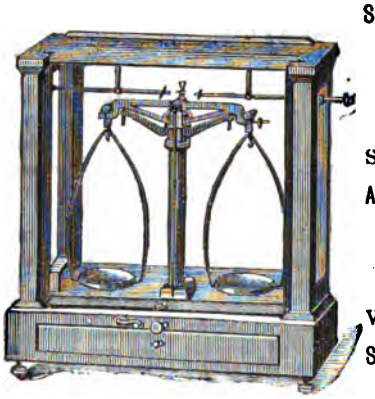

FIG. 3*a*.

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THE CHEMICAL NEWS.

VOL. LXIX., No. 1796.

ON THE METALLURGY OF LEAD.*

By J. B. HANNAY.

In this paper the author gave an exhaustive account of the researches by which he has thrown some light on the chemistry of the metallurgy of lead. After investigating the relations of lead and sulphur, and showing that there exists only one sulphide of lead, and that the supposed lower sulphides are mixtures of metallic lead with the mono-sulphide, the author shows that all such mixtures may be fractionated into their two ultimate components by repeated fusion and crystallisation.

An examination of the chemical reasons given by accepted authorities for the production of lead in the furnace was next undertaken, and it was shown that the reaction which is supposed to account for the smelting of galena has no existence. The theory was that a portion of the sulphide of lead is oxidised to sulphate, and this reacts with a portion of the unaltered sulphide to produce lead; thus $PbS + PbSO_4 = 2Pb + 2SO_2$.

It was found that $PbSO_4$ and PbS mixed and exposed in a closed vessel to the temperature of a lead furnace did not react, as the temperature was too low for the fusion of either; and even when melted together at a temperature far above that of the smelting furnace, the above reaction did not ensue, but a very complex reaction took place, which varied according to temperature, but which in its simplest form and when carried to a conclusion yielded the following reaction:—

$$2PbS + 2PbSO_4 = Pb + 2PbO + PbS_2O_2 + 2SO_2.$$

The substance PbS_2O_2 is a new volatile compound of lead, and is formed in greater or less quantity whenever PbS and SO_2 are brought in contact at a high temperature, and is the substance which causes the well-known "lead fume."

A large part of the paper is occupied in tracing all the variations of this reaction, and also the substances formed by the interaction of the products of decomposition, which accumulate in the residue.

The formation of slag is shown to be due to a molecular compound, PbS.PbO, which is the lead member of a series of compounds of PbS, with oxides of which the volatile body $PbS.SO_2$ or $PbSO_2$ is also one. Others are formed by combination with water-vapour and with the oxides of carbon, and they are also volatile. They all dissociate on cooling, and even the lead member PbS.PbO, which can be shown to be transparent at a high temperature, becomes opaque on cooling, and the PbO may be dissolved out by ammonium acetate, leaving the PbS in fine black powder.

By an exhaustive set of experiments on mixtures of all the substances involved in the furnacing of lead ore, the author shows that lead is not produced by any direct reaction of any two of the products. For instance, some authors state that the action is one of $PbSO_4$ dissolved in fused PbO on the unaltered PbS, and although this is possible as far as temperature is concerned, yet the action does not produce metallic lead, but litharge as represented by the equation $SPbSO_4 + PbS = 4PbO + 4SO_2$.

The author investigates the reduction of sulphate of lead by carbon, as in the blast furnace smelting, and goes minutely into the formation of slags. An examination of the action of air on galena at different temperatures shows that it changes with difference of temperature and fineness of the particles, but that it is reduced to simplicity at the melting-point of galena, and is then represented by the equation $2PbS + O_2 = Pb + PbS_2O_2$, so that exactly one-half of the lead in the ore is obtained in the metallic state, and one-half is volatilised as PbS_2O_2.

Sufficient data were collected to form an entirely new explanation of the action going on in smelting lead. It really amounts to a burning-out of the sulphur till a low sulphurised material is obtained and some PbO formed. On cooling this a little, separation into lead and its mono-sulphide takes place, and on raising the temperature lead flows away free, and oxygen is absorbed and slag is formed.

It is clear that a great deal depends on the skill of the men conducting such an operation.

Lead smelting may be summed up by the formula—

$$24PbS + 22O_2 = 17Pb + \underbrace{2(PbS.PbO) + PbSO_4}_{\text{Slag.}} + \underbrace{2PbS_2O_2 + 17SO_2}_{\text{Fume.}},$$

which represents the best results obtained, viz., 66 per cent lead, 12 per cent slag, and 6 per cent fume, but slag often amounts to 14—16 per cent and fume to 12 per cent according to the character of the ore.

Slag and fume are the two evils of the present method of smelting lead ores, and the author proposes a new method founded upon the formation of the new volatile oxysulphide which he has discovered. When excess of air is passed through and over molten galena, the compound PbS_2O_2 is oxidised, and instead of—

$$2PbS + O_2 = Pb + PbS_2O_2,$$

we have—

$$2PbS + O_6 = Pb + PbSO_4 + SO_2,$$

and this $PbSO_4$ is of extreme purity and forms an excellent white pigment.

The silver is concentrated in the residual lead, which may be converted into litharge by continuing the blowing, and the silver concentrated to a rich bullion.

* Abstract of a Paper read before the Institute of Mining and Metallurgy, April 18, 1894.

ON SIEMENS-MARTIN STEEL.

By SERGIUS KERN, M.E., St. Petersburg.

MANY engineers advocate the previous melting in a cupola of the spiegeleisen, which is at present usually added in a solid form, as a final addition to the metallic bath, when medium or hard Martin steel is produced; and these metallurgical engineers are quite correct in their views, and we were always surprised that steel-works somehow overlooked this question. Our observations, made several years ago at the Obouchoff Steel Works, St. Petersburg (properly ordnance works), run as following:—

In preparing medium hard steel for the casting of ingots intended for the forging of the parts of guns, sometimes 12—17 cwts. of spiegeleisen were added to a charge of 10 tons weight of the cold metal charged. The spiegeleisen was placed as ordinarily on the banks of the furnace, and after ten to fifteen minutes shifted into the metallic bath. Now let us see what may happen:—

1. The workmen in a hurry (this often occurs when all is ready for casting) shift down the lumps of spiegeleisen not sufficiently heated through. This, firstly, cools the bath in several places and gives rise to *nests* of harder metal in the ingot and next in the forged article. Of the occurrence of such a fact we are certain. Even the pouring of the ready steel in the ladle, and from the latter into the moulds, does not destroy the *nests*—why, we are rather ignorant. But in boring long gun tubes from such forged material, we may remark that the resulting work

of boring proceeds in jumps. Several engineers told us the same. All goes right, but suddenly no cutter can take the metal. The article must be sent for a second annealing to the annealing shop. After some trouble the hard part is passed now over by the cutter, and the boring again goes smoothly on, when very often another hard part is met, and so on. Numerous analyses proved the following:—

Sample.	Carbon.
Average for steel tubes	0·60 per cent.
Hard parts in tubes	1·15 ,,

In crucible steel such things also happen when, during the casting, some crucibles with raw steel happen to be added between the crucibles containing good steel melted throughout.

2. In the preparation of medium hard steel it is always possible to meet with a thick sticky slag. Cold pieces of spiegeleisen, after the bath has been raked, float up and adhere in different places, forming the above-mentioned *nests* of hard metal. It results that the slags must be kept fluid, which is an ordinary custom in the preparation of Martin steel.

We strongly advise the use of a cupola for the melting of spiegeleisen for the carburisation of the Martin steel. For furnaces of small capacity a crucible coke furnace may be erected at the side of the chief chimney at a small expense; thus the melting of the additions may be compact and neat.

REPORT OF COMMITTEE ON DETERMINATIONS OF ATOMIC WEIGHT PUBLISHED DURING 1893.*

By F. W. CLARKE.

(Continued from p. 190).

Thallium.

LEPIERRE (*Bull. Soc. Chim.*, 3, ix., 166, March 20, 1893) has re-determined the atomic weight of this metal by several distinct methods. First, by the electrolysis of thallous sulphate in presence of an excess of ammonium oxalate, weighing first the sulphate and then the metal obtained. The latter was dried and weighed in an atmosphere of hydrogen. The corrected weights and results are as follows:—

Wt. Tl_2SO_4.	Wt. Tl_2.	At. wt. Tl (O=15·96).
1·8935	1·5327	203·52
2·7243	2·2055	203·67
2·8112	2·2759	203·69

Secondly, a weighed quantity of crystallised thallic oxide was converted by means of sulphurous acid into thallous sulphate, which was then subjected to electrolysis as in the preceding series. The results are subjoined.

Wt. Tl_2O_3.	Wt. Tl_2.	At. wt. Tl.
3·2216	2·8829	203·76
2·5417	2·2742	203·53

In the third series of experiments a definite quantity of thallous salt was fused in a polished silver crucible with ten times its weight of absolutely pure caustic potash. Thallic oxide was thus formed, which was washed with water and alcohol under various precautions, dried at 100°, and finally weighed in the original crucible.

		At. wt. Tl.
3·1012 Tl_2SO_4 gave ..	2·8056 Tl_2O_3	203·57
2·3478 ,, ,, ..	2·1239 ,,	203·44
2·7591 $TlNO_3$,, ..	2·3649 ,,	203·73

Finally, crystallised thallic oxide was reduced in a stream of hydrogen, and the water so formed was collected and weighed.

Wt. Tl_2O_3.	Wt. H_2O.	At. wt. Tl.
2·7873	0·3301	203·54
3·9871	0·4716	203·82
4·0213	0·4761	203·00

The mean of the eleven figures given for thallium is 203·57, but stated by the author as 203·62. If O = 16 this becomes Tl = 204·08; and with O = 15·88, Tl = 202·55. It will be observed that the values found in the individual experiments vary among themselves through a range of over eight-tenths of a unit, and that, therefore, the final mean result is entitled to little consideration. M. Lepierre is evidently unfamiliar with the determinations of his predecessors; for, quite ignoring the admirable work of Crookes, he speaks of the currently accepted value for Tl as resting without proof upon the calculations of Meyer and Seubert. He also neglects to state whether his weighings were reduced to vacuum standards, and he gives no evidence bearing upon the absolute purity and definiteness of the several compounds weighed. The metallic thallium which served as a starting point for the investigations seems to have been carefully purified.

The Composition of Water by Volume.

The volume ratio between H and O in water, which controls the atomic weight of oxygen as deduced from its density, has been re-determined by Scott (*Proc. Roy. Soc.*, liii., 130; read March 23, 1893). The report published is only in abstract, but the subjoined values for the ratio, H_2 : O, are given.

2·0020
2·0024
2·0026
2·0030
2·0022
2·0025
2·0029
2·0023
2·0028
2·0017
2·0022
2·0028
Mean .. 2·00245, ± 0·00007.

Combining this mean with the density ratio—

O : H : : 15·882 : 1 (Rayleigh),

gives for the atomic weight of oxygen the value 15·862.

Scott gives mean results of several other series of experiments, but only this one in detail. The hydrogen was obtained from palladium hydride, and the oxygen from silver oxide. With only an abstract available, the work done cannot be critically compared with Morley's.

The Density of the Principal Gases.

These data, as determined by Lord Rayleigh (*Proc. Roy. Soc.*, liii., 134; received March 4, 1893), having important bearing upon atomic weights, fall properly within the scope of this report. Full details are given as to the apparatus used, and all corrections are applied; such, for instance, as for the difference in volume of the glass globes when filled or exhausted, for the value of gravity at the laboratory in latitude 51° 47", &c. The final results are as follows, with air as unity.

H	0·06960
N	0·97209
O	1·10535

The weights in grms. per litre are:—

H	0·09001
N	1·25718
O	1·42952
Air	1·29327

* From the *Journal of the American Chemical Society*, xvi., No. 3.

Two of these constants have also been re-measured by Leduc (*Comptes Rendus*, cxvii., 1072), who gives the following weights for one litre each :—

Air	1·29315
N	1·2570

(To be continued).

THE QUESTION OF THE OCCURRENCE OF HYDROGEN PEROXIDE IN ATMOSPHERIC AIR AND IN ATMOSPHERIC WATERS.*

By EM. SCHÖNE.

(Concluded from p. 186.)

Finally, Iloswa contends that his chief experiment (the second) was undertaken at a time particularly favourable for the possible occurrence of ozone and hydrogen peroxide as it abounded in showers and thunderstorms, and as the lightning once even struck a conductor adjoining the window of his laboratory. I am of opinion that it was *not* an especially favourable time, especially for ozone, as lightning produces not this substance, but the oxides of nitrogen, nor for the formation of peroxide, since on the condensation of watery vapour to rain clouds the peroxide is condensed also, whilst the residue left in the air in the state of vapour is chiefly carried down by the falling rain-drops—a fact which I have sufficiently shown in my former researches (*Berichte*, vii., 1705; and xi., 563).

On the ground of these considerations I must conclude that this experiment, so especially valued by Iloswa, proves absolutely nothing.

As the atmospheric downfall gives simultaneons reactions with the reagents characteristic for hydrogen peroxide, and on the other with those characteristic for nitrous acid, we might possibly assume that there exists in the air an unknown oxidising agent from which are obtained both the reactions of peroxide and those of nitrous acid, though it is neither of these compounds. If this were the case there must evidently exist a parallelism between the intensities of the reactions actually obtained in one and the same specimen—on the one hand with potassium iodide, starch, and ferrous sulphate or guiacum and diastase, and on the other hand with the reagents of Griess.

In order to test this assumption I have in the two last years frequently collected rain and examined it with reagents of both kinds. It resulted that in many cases slight reactions were obtained with the reagents for peroxide in specimens in which Griess's test reacted very strongly and inversely; in other cases the latter were very faint, *i.e.*, indicated proportions of nitrous acid which fell below the limit of the recognition of peroxide, whilst at the same time the tests for the latter gave very decided reactions. This proves that there exists no such parallelism, and that the specimens of rain examined contained both hydrogen peroxide and nitrous acid (in the state of a neutral salt).

These observations furnish at the same time a further argument to prove that the reactions from which we infer the presence of hydrogen peroxide cannot be due to nitrous acid.

I must, however, not conceal that Iloswa makes a small concession. He says: "If we wish to draw a conclusion from these facts we shall form a sole opinion that there is in the air no ozone and no hydrogen peroxide, or, making a concession to tradition, that in the worst case if these substances exist that we have hitherto no certain means of proving their existence in the air." This last utterance gives us room to hope that Iloswa on a renewed careful examination of the subject may alter his opinion.

On my part I adhere to my opinion of the existence of hydrogen peroxide in the atmosphere, as well as to all the conclusions which I have drawn from my former observations and investigations.

* *Berichte der Deutschen Chemischen Gesellschaft*, xxvi., p. 3011.

BIOGRAPHY AS SHE IS WRIT IN FRANCE.

Monsieur Hippolyte Cocheris, Attaché à la Bibliothèque Mazarine, Membre de la Société Impériale des Antiquaires de France, in a "Notice sur les Travaux de la Société Smithsonienne de Washington" (Paris, 1857), makes the following statement :—

"Lord James Smithson était fils naturel de Georges IV. La position dans laquelle il se trouvait à Londres s'engagea à s'expatrier, il quitta l'Angleterre et se rendit aux Etats-Unis. Sa fortune qui était considérable, lui ouvrit les portes de tous les salons de New York et de Washington, où il résida jusqu'à sa mort, arrivée en 1837." (Page 2).

The facts are that Smithson was a natural son of Hugh Smithson, first Duke of Northumberland. He never visited America, and is thought to have had not even a correspondent there. He died in the south of France, October, 1829.

This French biographer of the chemist writes in a friendly and even complimentary way of the Institution, but seems to have taken pains to invent fictions rather than give facts easily obtained. He reminds us of that other French writer who represents Joseph Priestley making the acquaintance of Jefferson Davis in America, and dying in 1804. Of this, however, I have written before.—H. C. B.

THE ATOMIC WEIGHT OF PALLADIUM.*

By EDWARD H. KEISER and MARY B. BREED.

In an investigation by one of us, published in 1889 (*Am. Chem. Journ.*, xi., 398), upon the atomic weight of palladium, it was found that palladium diammonium chloride, $Pd(NH_3Cl)_2$, is a much more suitable compound for the determination of the atomic weight of this metal than the double chloride of palladium and potassium that had previously been used by Berzelius for this purpose. The palladammonium chloride is a compound that can be prepared in a state of great purity; it can be thoroughly dried without undergoing decomposition; it is not hygroscopic, and the amount of palladium in it can be accurately determined by heating it in a current of hydrogen, whereby ammonium chloride is volatilised and metallic palladium remains behind. As the result of nineteen determinations made in this way upon different preparations of the compound, the number 106·35 was obtained for the atomic weight. This number was calculated directly from the weights of the substances in air. If the weights be reduced to a vacuum, then the value of the atomic weight becomes 106·27. Recently several investigators have worked upon this subject and have published results, some of which are considerably higher and others decidedly lower than the number 106·3.

Thus, Bayley and Lamb (*J. Chem. Soc.*, 1892, lxi., 745), after examining a number of palladium compounds for the purpose of devising a new method of determining the atomic weight, have adopted the method described above, namely, reduction of palladammonium chloride in a current of hydrogen, and find as the mean of ten determinations the value 105·46. From a series of chlorine determinations in the compound they obtained the number 106·37, but this they regarded as less accurate than the other.

* From the *American Chemical Journal*, xvi., No. 1.

Keller and Smith (*Am. Chem. Journ.*, xiv., 423) have also published the results of their determinations of the atomic weight of palladium. They, too, have determined the ratio of palladium to palladammonium chloride. Weighed quantities of the compound were dissolved in dilute ammonia, and the solution subjected to electrolysis in platinum dishes containing a deposit of metallic silver. The increase in weight of the dish was taken as the weight of the palladium deposited. Nine determinations were made, from which the number 106·91 was obtained for the atomic weight.

Joly and Leidié (*Comptes Rendus*, 1893, cxvi., 146) have made some preliminary experiments on the atomic weight of palladium. Weighed quantities of the double chloride of potassium and palladium were dissolved in water, and the metal precipitated by electrolysis. From the ratio of palladium to potassium-palladium chloride they obtain the number 105·44 for the atomic weight.

The different determinations, then, stand as follows:—

Berzelius,	1829	106·2
Keiser,	1889	106·3
Bayley and Lamb,	1892	105·5
Keller and Smith,	1892	106·9
Joly and Leidié,	1893	105·4

As these recent determinations differ from one another by as much as one and a half units, it seemed desirable to take up the work again and to endeavour to establish this constant with a greater degree of certainty than has yet been attained. We have endeavoured in the first place to find some compound of palladium that could be vapourised, and therefore subjected to fractional distillation. For, as Stas has shown, it is only the substances that can be vapourised that can be obtained in a high state of purity.

Distillation of Palladium Chloride in a Current of Chlorine.

We have found that palladium dichloride, $PdCl_2$, can be distilled at a low red heat in a current of chlorine. For the purpose of obtaining palladium chloride and purifying it by distillation, spongy palladium, obtained by the reduction of palladium diammonium chloride—the metal remaining from the atomic weight determinations of 1889—was placed in a thin layer in one end of a combustion-tube. In the middle of the tube there was a constriction which prevented liquid from flowing from one end to the other when the tube was in a horizontal position. The end of the tube containing the palladium was connected with an apparatus furnishing a stream of dry chlorine. The tube was placed in a combustion-furnace and so arranged that that portion of the tube containing the palladium could be heated to a bright red heat. The chlorine was prepared from hydrochloric acid and manganese dioxide, and after washing with water was led through two bottles containing concentrated sulphuric acid. The gas after passing through the tube containing the palladium, and before escaping into the air, was conducted through water contained in two wash-bottles to remove palladium chloride from it. After the chlorine had displaced all the air in the apparatus, that portion of the tube containing the palladium was heated in the furnace. When the temperature began to approach a low red heat the metal combined rapidly with the chlorine. Soon it began to glow, and in a few moments the entire quantity of metal had been converted into chloride. The heating was continued and a slow current of chlorine passed through the tube. The palladium chloride melted and became a dark liquid, and soon a red sublimate began to appear in the cold portion of the tube. The heating was continued, and after a time the entire cross-section of the tube for a length of several inches became filled with minute dark red needle-shaped crystals. The molten chloride in the front portion of the tube appeared to be boiling, as gas-bubbles were slowly evolved from it. After a considerable quantity of the crystalline sublimate had been prepared in this way, the tube was allowed to cool and the crystals removed. An analysis showed that they were palladium dichloride, $PdCl_2$.

0·2011 grm. gave on reduction in a current of hydrogen 0·0804 grm. Cl.

	Calculated for $PdCl_2$.	Found.
Cl	40·01	39·98

When the crystals are heated in a stream of chlorine they melt and form, when cold, a dark red crystalline mass consisting of dichloride mixed with monochloride. The crystals are deliquescent and absorb moisture in the air.

Several distillations of palladium chloride in a current of chlorine were now made, and a quantity of the distilled chloride weighing a little more than 10 grms. was obtained. This was re-distilled in the same manner, and of the distillate the more volatile and the least volatile portions were rejected and only the middle portion used for the subsequent work.

We hoped at one time to use the dichloride directly for the determination of the ratio of palladium to chlorine, but owing to its deliquescent nature and the fact that when melted the dichloride is partially converted into monochloride, we abandoned experiments in this direction, and decided to convert the dichloride into palladium diammonium chloride. For this purpose the re-distilled chloride was dissolved in distilled water to which a few drops of hydrochloric acid had been added. Ammonia was added gradually, and the solution warmed upon the water-bath until the flesh-coloured precipitate had dissolved. The filtered solution was diluted with a large volume of water, and into the dilute solution a current of pure hydrochloric acid gas was passed. The palladammonium chloride thus formed was washed repeatedly by decantation, and finally upon the filter. It was then dissolved in dilute ammonia and re-precipitated with hydrochloric acid gas, thoroughly washed, and then dried in desiccators.

(To be continued.)

THE DETERMINATION OF POTASH.*

Method of Lindo-Gladding.

1. *In Superphosphates.*—Boil 10 grms. with 300 c.c. of water thirty minutes. To the hot solution add ammonia in slight excess, and then a sufficient quantity of ammonium oxalate to precipitate all the lime present; cool, and make up to 500 c.c., mix thoroughly, and filter through a dry filter; take 50 c.c. corresponding to 1 grm., evaporate nearly to dryness, add 1 c.c. of dilute sulphuric acid (1 to 1), evaporate to dryness, and ignite to whiteness. As all the potash is in form of sulphate, no loss need be apprehended by volatilisation of potash, and a full red heat must be maintained until the residue is perfectly white. This residue is dissolved in hot water, plus a few drops of hydrochloric acid, and a slight excess of platinum solution is now added. This solution is then evaporated to a thick paste in a small dish, and 80 per cent alcohol added. In evaporating special precaution should be taken to prevent absorption of ammonia. The precipitate is washed thoroughly with alcohol by decantation and on the filter, as usual. The washing should be continued even after the filtrate is colourless. Ten c.c. of the ammonium chloride solution, prepared as hereafter directed, are now run through the filter, or the washing may be performed in the dish. The 10 c.c. will contain the bulk of the impurities, and are thrown away. Fresh portions of 10 c.c. of the ammonium chloride are now run through the filter

* Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (American) at its Meeting at Chicago, August, 1893.

several times (five or six). The filter is then washed thoroughly with pure alcohol, dried, and weighed as usual. Care should be taken that the precipitate is perfectly soluble in water. The platinum solution used contains 1 grm of metallic platinum in every 10 c.c. To prepare the washing solution of ammonium chloride, place in a bottle 500 c.c. of water, 100 grms. of ammonium chloride; shake till dissolved. Now pulverise 5 or 10 grms. of potassium platinic chloride, put in the bottle, and shake at intervals for six or eight hours; let settle over night, then filter off the liquid into a second bottle. The first bottle is then ready for preparation of a fresh supply when needed.

2. *Muriates of Potash.*—In the analysis of these salts an aliquot portion containing 0·5 grm. is evaporated with 10 c.c. of the platinum solution and a few drops of hydrochloric acid, and washed as before.

3. *Sulphate of Potash, Kainite, &c.*—In the analysis of kainite, dissolve 10 grms. of the pulverised salt in 300 c.c. of boiling water, add ammonia to slight excess, then a sufficient quantity of ammonium oxalate to throw down all lime present; cool, and make up to 500 c.c., mix thoroughly, and filter on a dry filter; take 25 c.c., corresponding to 0·5 grm., and proceed to remove the ammonia, as in the analysis of superphosphates; dissolve the residue in hot water plus a few drops of hydrochloric acid, and add 15 c.c. of platinum solution. In the analysis of high-grade sulphate and of double-manure salt (potassium sulphate, magnesium sulphate, containing about 27 per cent of potassium oxide), make up the solution as above, but omit the precipitation, evaporation, &c.; take an aliquot part equal to 0·5 grm. and add 15 c.c. of platinum solution. In all cases special care must be taken in the washing with alcohol to remove all the double platinum-sodium chloride if present. The washing should be continued some time after the filtrate is colourless. Twenty-five c.c. of the ammonium chloride solution are employed instead of 10 c.c., and the 25 c.c. poured through at least six times to remove all sulphates and chlorides. Wash finally with alcohol; dry and weigh as usual.

4. *Organic Compounds.*—In case the potash is contained in organic compounds, like tobacco stems, cotton-seed hulls, &c., weigh out 10 grms., saturate with strong sulphuric acid, and ignite in a muffle to destroy organic matter. Add a little strong hydrochloric acid to moisten the mass, and warm slightly so as to loosen it in the dish. Proceed then as in 1.

Alternate Method for Potash.

Take 10 grms. of the prepared sample, boil for ten minutes with 200 c.c. of water, and, after cooling, and without filtering, make up to 1000 c.c. and filter through a dry filter. If the sample has 10 to 15 per cent of potassium oxide (kainite), take 50 c.c. of the filtrate; if from 2 to 3 per cent of potassium oxide (ordinary potash fertilisers), take 100 c.c. of the filtrate. In each case make the volume up to 150 c.c., heat to 100°, and add, drop by drop with constant stirring, slight excess of barium chloride, without filtering; in the same manner add barium hydrate in slight excess. Filter while hot, and wash until the precipitate is free of chlorides. Add to the filtrate 1 c.c. of strong ammonium hydrate, and then a saturated solution of ammonium carbonate until the excess of barium is precipitated. Heat; add now, in fine powder, 0·5 grm. pure oxalic acid or 0·75 grm. of ammonium oxalate. Filter; wash free of chlorides, evaporate the filtrate to dryness in a platinum dish, and ignite carefully over the free flame below red heat until all volatile matter is driven off.

The residue is now digested with hot water, filtered through a small filter, and washed with successive small portions of water until the filtrate amounts to 30 c.c. or more. To this filtrate, after adding 2 drops of strong hydrochloric acid, are added in a porcelain dish, 5 to 10 c.c. of a solution of 10 grms. of platinic chloride in 100 c.c. of water. The mixture is now evaporated on a water-bath to a thick syrup, as above, treated with 80 per cent alcohol, washed by decantation, collected in a Gooch crucible, or other form of filter, washed with strong alcohol, afterwards with 5 c.c. of ether, dried for thirty minutes at 100°, and weighed.

It is desirable, if there be an appearance of foreign matter in the double salt, that it should be washed, according to the previous method, with 10 c.c. of the half-concentrated solution of ammonium chloride, which has been saturated by shaking with potassium platinic chloride.

Factors.

The use of the factors 0·3056 for converting potassium platinic chloride to potassium chloride, and 0·19308 for converting to potassium oxide is continued.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 15th, 1894.

Dr. Armstrong, President, in the Chair.

Messrs. William G. Boul, Frank Evershed, and G. N. Huntly were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. George Dixon, Trinity College, Cambridge; Nicholas Eumorfopoulos, 1, Kensington Park Gardens, W.; G. S. Newth, 29, Mount Park Road, Ealing; Alfred Nixon, 14, Entwistle Street, Moss Side, Manchester; Herbert Harold Robjohns, King's School, Pontefract, Yorks; George Ryce, B.A., Rathmore Place, Cork; John George Spenzer, M.D., Ph.D., 370, Central Avenue, Cleveland, U.S.A.; Arthur Swainson, The Grammar School, Beverley; Edward Cumming Thompson, 5, Gubyon Avenue, Herne Hill, S.E.

Of the following papers those marked * were read:—

*120. "*Formaldoxime.*" By Wyndham R. Dunstan, F.R.S., and A. L. Bossi, B.Sc., Ph.D.

Our knowledge of this compound, the first member of the series of paraffinic aldoximes, is very limited, being in fact represented only by the observations made a few years ago by Scholl (*Ber.*, xxiv., 573), who found that the chief product of the interaction of formaldehyd and hydroxylamine was a white amorphous solid, which behaved as a polymeride of formaldoxime. The aldoxime itself Scholl was only able to study as a solution, obtained by heating the polymeride with certain liquids, and as a gas obtained by heating the dry polymeride. He showed that the substance in these two forms has a molecular weight corresponding with the formula $CH_2{:}NOH$, that it is a powerful reducing agent, and in its other properties behaves as an aldoxime.

The authors have obtained formaldoxime as a colourless, highly refractive liquid, boiling between 84—85°, by extracting with ether a warm freshly prepared mixture of aqueous formaldehyd and hydroxylamine (hydroxylamine hydrochloride with the calculated amount of sodium carbonate), and then fractionally distilling the ethereal solution. All attempts to crystallise the liquid have failed. When cooled it quickly changes into the solid polymeride, and even at the ordinary temperature it cannot be kept for long without polymerisation taking place. It has a slight curious odour, which is difficult to describe, and it burns with a livid yellow flame, producing much hydrogen cyanide, $CH_2NOH = H_2O + HCN$. A determination of the molecular weight of the liquid by Raoult's method, using acetic acid as the solvent, gave a result corresponding with the formula $CH_2{:}N{\cdot}OH$.

Formaldoxime undergoes quantitative hydrolysis into formaldehyd and hydroxylamine when it is digested with

cold concentrated hydrochloric acid, but when it is heated with dilute acids, formic acid and ammonia are also produced, owing to the previous conversion of some of the aldoxime into formamide, $HCONH_2$, a mode of isomeric change which is characteristic of these aldoximes.

Formaldoxime readily decomposes into its nitrile (hydrogen cyanide) and water when it is heated with aqueous alkalis, or when it is acted on by acetic chloride. It forms unstable derivatives with the alkali metals; the sodium derivative, CH_2NONa, is crystalline; it explodes when heated, and very readily loses water, becoming sodium cyanide.

When warmed with aqueous solutions of salts of silver, gold, copper, and mercury, formaldoxime acts as a powerful reducing agent. With cold aqueous copper sulphate it furnishes a dark green solution, which soon deposits crystals of a remarkable copper salt, and these, when kept, spontaneously evolve nitric oxide. This compound is still under examination.

When dry hydrogen chloride is led into the well dried ethereal solution of formaldoxime, the *hydrochloride* separates as an amorphous solid, which, however, may be readily crystallised from its solution in a mixture of alcohol and ether. When analysed, the well defined prismatic crystals (m. p. 136°) furnished data corresponding with the formula $(CH_2NOH)_3HCl$.

This remarkable salt, which can easily be obtained pure, constitutes a convenient source for the preparation of pure formaldoxime. It dissociates into the aldoxime and hydrochloric acid when it is dissolved in water, and if the solution is neutralised, pure formaldoxime may be recovered by distillation. The salt dissolves when warmed with aniline, and the formaldoxime can then be distilled from the mixture. A similar crystalline *hydrobromide*, $(CH_2NOH)_3HBr$, m. p. 120°, and also a *hydroiodide*, have been prepared.

By the spontaneous evaporation of a mixture of acetic anhydride and an ethereal solution of formaldoxime, a stable crystalline *acetformaldoxime*, $CH_2NO(CH_3CO)$, was obtained. A molecular weight determination, using acetic acid as the solvent, gave a result corresponding with the formula $(CH_2NO{\cdot}CH_3CO)_3$. It melts sharply at 133°. On hydrolysis it yields chiefly formaldehyd, acetic acid, and hydroxylamine. A crystalline *benzoic derivative* of formaldoxime was also prepared. This is a stable substance melting at 168·5°.

Having regard to the theoretical importance which attaches to a complete knowledge of the properties of formaldoxime, the authors are further investigating some of the compounds now described, and are preparing other derivatives.

*121. "*Derivatives of Camphene containing Halogens.*" By J. E. MARSH and J. A. GARDNER.

Methods are described for obtaining such derivatives (1) by the action of halogens on camphene-phosphonic acids, (2) by the hydrolysis of substituted camphene-phosphonic acids, (3) by direct substitution of hydrogen in the hydrocarbon, (4) by the splitting off of halhydride from additive compounds. This last method affords a means of obtaining substituted camphenes from camphor. According to Pfaundler, if the dichloride is heated, it loses hydrogen chloride, yielding a compound of the formula $C_{10}H_{15}Cl$, the existence of which has, however, been denied by Spitzer. The authors find that chlorocamphene is readily obtained from the product of the action of phosphorus pentachloride on camphor, when it is boiled with aniline, or better, with quinoline. The chlorocamphene thus obtained is a very stable compound, remaining unchanged when heated at 250° with quinoline. It distils at 198—200°, and is slightly lævorotatory. On distillation it collects in the receiver as a solid of low melting-point.

The compound of the formula $C_{10}H_{16}Cl_2$ distils almost unchanged. But the distillate is found to have a much greater rotatory power than the original substance; and the rotatory power is found to increase on successive distillations: thus a substance having a rotatory power $[\alpha]_D = -9°$, after one distillation had a rotatory power of -19, after two of $-30°$, and after three of $-35°$. The explanation of this effect has yet to be found: it may be the result of an isomeric change.

Bromocamphene may be obtained from camphor by mixing phosphorus trichloride and bromine in molecular proportions, and gradually adding camphor. At first a considerable amount of a red solid, probably a compound of the formula $C_{10}H_{16}OBr_2$, is formed, but after a time this disappears and a clear almost colourless liquid is obtained. From this a new substance, represented by the formula $C_{10}H_{16}Br_4$, was isolated; this forms large colourless crystals, resembling dipentene tetrabromide, which melt at 171°. The compound $C_{10}H_{16}Br_2$ was not obtained.

The action of chlorine on camphene in presence of alcohol is somewhat violent, and does not only afford chlorocamphene, but yields a number of liquid chlorinated products which are difficult to separate. The product, boiling at about 220°, nearly corresponds to a chlorocamphene. The boiling-point is, however, 20° higher than that of the chlorocamphene prepared from camphor.

*122. "*A Sulphate of Oxamide.*" By J. E. MARSH.

Oxamide is known to behave as a weak acid and to form salts with metallic oxides, but apparently it has not been observed to combine with acids to form salts. I find, however, that oxamide dissolves in strong sulphuric acid without decomposing, and, on adding water, it is precipitated apparently unchanged, as 92 and 94 per cent were thus recovered in two experiments. The solution of oxamide in strong sulphuric acid may be heated to above 140° without decomposition occurring, although when oxalic acid is heated with strong sulphuric acid, it decomposes briskly at 100°. In an experiment in which 2·5 grms. of oxamide, together with 10 c.c. of strong sulphuric acid, were heated at 100° on the water-bath, a solution was obtained, from which, on cooling, a quantity of large colourless transparent crystals were deposited. It was difficult to get the crystals free from adherent acid, as no solvent could be used to wash it away without instantly decomposing the compound; they were, therefore, filtered off and dried quickly with blotting paper. Analysis showed the crystals to be disulphate of oxamide, $(CONH_2H_2SO_4)_2$. Fuming nitric acid dissolves the crystals without precipitating oxamide, the solution undergoing violent decomposition after standing a few minutes.

Oxamic acid, $CO(NH_2){\cdot}COOH$, also dissolves in strong sulphuric acid, and the solution deposits crystals on cooling. Water does not cause any precipitation in this solution.

Oxamethane, $CO(NH_2){\cdot}CO_2Et$, is completely hydrolysed by dissolution in strong sulphuric acid, barium oxamate, $(NH_2C_2O_3)_2Ba+3H_2O$, being obtained from the liquid on neutralising it with barium carbonate.

*123. "*Fluoplumbates and Free Fluorine.*" By BOHUSLAV BRAUNER, Ph.D.

By substituting fluorine for oxygen or an acid radicle in several compounds of tetrad lead, by acting on the oxide with fluorhydric acid and potassium hydrogen fluoride, the salt $3KF{\cdot}HF{\cdot}PbF_4$ was obtained as a first member of the series of triple plumbic fluorides (*fluoplumbates*). This salt crystallises in colourless needle-shaped forms, analogous in composition to, and isomorphous with, the monoclinic triple stannic fluoride (fluostannate), $3KF{\cdot}HF{\cdot}SnF_4$, obtained by Marignac. On heating at about 230° the lead salt loses hydrogen fluoride, and at a higher temperature fluorine is evolved. On attacking the triple fluoride with concentrated sulphuric acid, a lemon-coloured substance is obtained, which appears to be *lead tetrafluoride*.

124. "*The Action of Nitrosyl Chloride on Unsaturated Compounds.*" By WILLIAM A. TILDEN, F.R.S., and MARTIN O. FORSTER,

The authors have continued the work begun by Tilden and Sudborough (*Trans.*, 1893, 479), and have extended the investigation to unsaturated acids and several phenols and their ethers. Some unexpected anomalies have been encountered, inasmuch as many unsaturated compounds, which instantly unite with bromine, are found to be indifferent to nitrosyl chloride or are attacked very slowly, forming chlorinated products instead of nitroso-chlorides. Thus, while phenylethylene (cinnamene) and diphenylethylene (stilbene) combine with nitrosyl chloride, phenanthrene and acenaphthylene do not, phenanthrene yielding a considerable quantity of chloro-substitution derivatives. Again, while the compounds obtained from the majority of the olefines behave like hydroximes, which, on hydrolysis, yield hydroxylamine, a number of the others—those from cinnamene, oleic acid, and anethol, for example—do not give hydroxylamine, neither do they afford Liebermann's test. These cases, therefore, require further investigation before the constitution of the "nitroso-chlorides" can be regarded as settled.

125. "*Note on the Action of Nitrosyl Chloride on Amido-derivatives of Benzenoid Hydrocarbons.*" By WILLIAM A. TILDEN, F.R.S., and J. H. MILLAR.

This wide field of work has been explored rather rapidly, with the object of ascertaining the general nature of the interactions which nitrosyl chloride is capable of entering into with benzenoid amines. We are now in a position to state that in the great majority of cases nitrosyl chloride behaves towards these compounds as the chloride of nitrous acid, giving rise either to nitroso compounds or diazo-compounds. In a few cases only it produces the simple effect of chlorination.

Reserving details for a future communication, the following facts may be regarded as established. In applying the agent, the solvent used has been generally ether, which is very slowly attacked by it, even in daylight. In a few cases glacial acetic acid has been used. A low temperature is usually necessary.

Examples of Diazotisation.—Aniline in ether readily yields diazoamidobenzene, crystallising in characteristic form and melting at 97°.

Parachloraniline in ether gives *pp*-dichlorodiazoamidobenzene, melting at 126—127° (Griess gave the melting-point 125°, Meldola and Streatfield 130°, *Trans.*, liii., 670).

Paranitraniline gave *pp*-dinitrodiazoamidobenzene, m. p. 224°.

Orthonitraniline and *metanitraniline* give the corresponding very unstable diazochlorides.

Examples of the Formation of Nitroso-compounds.—Methylaniline yields methylphenylnitrosamine,—

$$C_6H_5N{\cdot}NO{\cdot}CH_3,$$

which separates from the cold ethereal solution in the form of the hydrochloride as a colourless crystalline mass.

Dimethylaniline gives dimethylparanitrosoaniline hydrochloride, from which the base $C_6H_4(NO){\cdot}N(CH_3)_2$, m. p. 85°, was prepared.

Diphenylamine.—Diphenylnitrosamine is obtained in brilliant nearly colourless crystals, m. p. 66·5.

Examples of the Formation of Diazoimides.—Phenylhydrazin.—The formation of the diazoimide by the action of nitrosyl chloride on the acetic acid solution of this base has already been described (*Trans.*, 1893, 256).

α-Naphthylhydrazine and *β-naphthylhydrazine* both yield the corresponding diazoimides as easily fusible compounds volatile in steam.

Example of Chlorination.—Acetanilide, dissolved in glacial acetic acid, yields, when saturated with nitrosyl chloride, parachloracetanilide, m. p. 173°, as the only product. By protracted action, the nitroso-compound, $C_6H_3Cl_2{\cdot}N{\cdot}NO{\cdot}C_2H_3O$, m. p. 142·5°, appears to be formed.

126. "*Action of Aluminium Chloride on Heptylic Chloride.*" A Correction. By F. STANLEY KIPPING, Ph.D., D.Sc.

It has been ascertained that the ketone of the composition $C_{14}H_{20}O$, referred to in a previous note (*Proc. Chem. Soc.*, 128, 208), is paraheptyltoluene,—

$$C_6H_{13}{\cdot}CO{\cdot}C_6H_4{\cdot}CH_3,$$

and that it is not formed from heptylic chloride alone, but by the normal interaction of the acid chloride and toluene in presence of aluminium chloride. The first communication was made in ignorance of the fact that toluene was present, and it was not until the constitution of the ketone had been determined that it was found that the "petroleum," which the author's assistant had employed as a diluent (and which had simply been shaken with sulphuric acid and then distilled), accidentally contained toluene. The facts that the product contained 14 atoms of carbon, and that its formation from heptylic chloride could be expressed by a simple equation, served to delay the discovery of the mistake.

On oxidation with dilute nitric acid the ketone yields a mixture of terephthalic and paratoluic acids, together with an oil—probably capronic acid. The sparingly soluble acid to which the composition $C_{13}H_{10}O_6$ was provisionally assigned, is therefore terephthalic acid, the previous analysis having given rather too much carbon and too little silver, owing, doubtless, to the presence of small quantities of paratoluic acid, which would not be easily detected. When the oxime of the ketone is heated at 100° with sulphuric acid, it is converted into a crystalline substance melting at 78—79°, which is shown to be *heptylparatoluidine*, $C_6H_{13}{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$, by the fact that on hydrolysis with chlorhydric acid at 180°, it yields heptylic acid and paratoluidine.

127. "*Oximidosulphonates or Sulphazotates.*" By EDWARD DIVERS, F.R.S., and TAMEMASA HAGA.

Among the sulphazotised potassium salts discovered by Fremy are two named *neutral sulphazotate* and *basic sulphazotate*, the former of which Raschig has shown to be a hydroxylamine-disulphonate or oximidosulphonate.

Fully confirming Fremy's observations, that his two salts are directly convertible into one another, the authors hold them to be as certainly salts of one acid—oximidosulphonic acid—as are the alkali orthophosphate salts of one acid. Accordingly, oximidosulphonic acid is a tribasic acid, of which the three known potassium salts have the formulæ—

$KON(SO_3K)_2$ — Raschig's salt.

$HON(SO_3K)_2$ — Fremy's neutral salt.

$HON(SO_3K)_2,KON(SO_3K)_2$ — Fremy's basic salt.

The authors have obtained three sodium salts, $Na_3NS_2O_7$, $Na_2HNS_2O_7$, and $Na_2HNS_2O_7{\cdot}2Na_3NS_2O_7$; the double salt of sodium not matching that of potassium. They have also prepared and analysed the barium salt, $Ba_3(NS_2O_7)_2$; the hydroxy-lead salt, $(HOPb)_3NS_2O_7$; and a great number of compound salts—of sodium and potassium and hydrogen with each other, and of these each with barium and with lead. They have also obtained strontium-sodium, strontium-potassium, calcium, and ammonium salts, besides compounds of dipotassium oximidosulphonate with potassium nitrate and with sodium chloride.

The neutral or two-thirds normal alkali salts, that is, dipotassium and disodium oximidosulphonates, are readily converted by hydrolysis into oxyamidosulphonate and sulphate; and the corresponding salts of copper, zinc, and other common metals are obtainable only in solution. These salts cannot be formed from the alkali salts, a fact observed by Fremy, but discredited by Claus. For example, copper sulphate and dipotassium or disodium oximidosulphonate can be mixed in solution and then crystallised out separately by evaporation: but the formation of copper and other salts in solution can be effected by interaction of their sulphates and lead or barium oximidosulphonate. Ammonium oximido-

sulphonates are also obtained from the lead or barium salt and ammonium carbonate.

Normal copper, manganese, zinc, and some other oximidosulphonates cannot exist, the attempt to form them resulting in the production of the two thirds normal salt in solution and a precipitate of copper or other hydroxide; thus copper sulphate, added so long as it occasions a precipitate to the normal sodium salt, leaves disodium oximidosulphonate in solution along with sodium sulphate. Barium chloride and lead acetate, which yield normal salts, precipitate these from the five-sixths normal potassium salt, and leave the dipotassium salt in solution, from which, after a little evaporation, it crystallises. Such facts as these were observed by Fremy, but his results were not accepted by Claus. They form an interesting part of the evidence that the neutral and basic sulphazotates are salts of one and the same acid.

Oximidosulphonates, likely to become an important source of hydroxylamine (Raschig) and of hyponitrites, have hitherto been obtained by most unproductive and uncertain methods, Raschig's patented process to some extent excepted. Fremy states that he passed sulphur dioxide into a solution of potassium nitrite and hydroxide, but he did not supply the necessary details. Claus did not find the process productive, but the authors find it to be nearly perfect, giving easily and uniformly 95 and 97 per cent of the calculated quantity, according as hydroxide or bicarbonate is employed. All that is essential is to pass sulphur dioxide into a solution containing potassium nitrite, and either potassium hydroxide or acid carbonate in single molecular proportions till lacmoid paper is reddened, keeping the mixture actively agitated and immersed in brine with ice floating in it. The mother-liquor is decanted, and the crystals drained dry.

The disodium salt is prepared in essentially the same way; but being exceedingly soluble, it has to be separated by evaporation. It, however, crystallises well, is an anhydrous salt, and can be preserved much better than the potassium salt. In consequence of its not falling out of solution during its preparation, some of it is destroyed by the sulphur dioxide, so that about one-tenth of the sodium nitrite gets converted into nitrilosulphonate. To allow for this, some sodium hydroxide or carbonate has to be used in excess of that indicated by the equation, $NaNO_2+NaOH+2SO_2$. Further, when the sulphur dioxide has been all passed in, the nitrilosulphonate has to be got rid of by hydrolysis into imidosulphonate, because its presence greatly endangers the existence of the oximidosulphonate.

The potassium oximidosulphonate, and also the sodium salt, but the latter only in very impure solution, may also be prepared by the action of metasulphites on nitrites. The potassium salt can, however, be quite easily prepared by this method from potassium nitrite, the yield being over 60 per cent of the possible quantity. The only condition for such success, besides that of preserving a low temperature, is to take somewhat more than 3 mols. of potassium metasulphite to 2 mols. of potassium nitrite. The mixed solutions are to be left some time ice-cold, and the mother liquor of the resulting crystals then decanted whilst still ice-cold. The salt is contaminated with nitrilosulphonate, and must be washed and recrystallised.

To prepare a solution of the disodium salt, 1 mol. proportion of sodium nitrite is mixed with 2 mol. proportions of metasulphite. Much nitrilosulphonate and normal sulphite are formed at the same time, and from these the sodium oximidosulphonate cannot be separated.

Alkali oximidosulphonates are all unstable, except in the absence of water. Those which are alkaline suffer partial reversion to nitrite and sulphite, and when by the interchange—

$$2Na_3NS_2O_7+H_2O=NaNO_2+Na_2SO_3+\\+NaHSO_3+Na_2HNS_2O_7,$$

the solution becomes acid, hydrolysis sets in and completes their decomposition. Those which are neutral or slightly acid to test paper soon undergo hydrolysis.

The fact of reversion of oximidosulphonate into nitrite and sulphite has until now escaped detection. This remarkable change is almost completed in presence of very concentrated solution of caustic potash, slowly in the cold, quickly on heating—

$$K_3NS_2O_7+2KOH=KNO_2+2K_2SO_3+H_2O.$$

Dry alkali oximidosulphonates, kept at temperatures a little over 100° in the air, slowly increase in weight by hydrolysing in atmospheric moisture.

Oximidosulphonates decompose suddenly when heated: the normal sodium salt just above 180°, according to the equation $2Na_3NS_3O_7=3Na_2SO_4+SO_2+N_2$, and the disodium salt at about 170°, partly in one way, partly in another, as shown by the equations—

$$2Na_2HNS_2O_7=Na_2SO_4+2NaHSO_4+SO_2+N_2,$$
$$8Na_2HNS_2O_7=3Na_2SO_4+5Na_2S_2O_7+\\+(NH_4)_2S_2O_7+SO_2+3N_2;$$

while the normal hydroxy-lead salt suffers reversion into hydroxy-lead nitrite, lead sulphite, and water—

$$(HOPb)_3NS_2O_7=(HOPb)NO_2+2PbSO_2+H_2O.$$

128. "*Derivatives of Tetramethylene.*" By W. H. Perkin, jun., F.R.S.

Some time since Freund and Gudeman (*Ber.*, xxi., 2692) endeavoured to obtain tetramethyleneamine,—

$$\begin{matrix}CH_2\cdot CH_2\\ |\quad\ |\\ CH_2\cdot CH\cdot NH_2\end{matrix},$$

from the amide of tetramethylene-carboxylic acid,—

$$\begin{matrix}CH_2\cdot CH_2\\ |\quad\ |\\ CH_2\cdot CH\cdot CONH_2\end{matrix},$$

by the action of bromine and potash, but without success

The reason for their failure appears to lie in the fact that the amide used by them (m. p. 138°) was impure, as, if the pure substance recrystallised from ether and melting at 153° be employed, the action proceeds normally.

Tetramethyleneamine is a colourless oil (b. p. 82°) possessing a powerfully basic smell resembling that of amylamine; it mixes with water, heat being evolved, and absorbs carbon dioxide with avidity.

The *hydrochloride*, C_4H_9NHCl, crystallises from alcohol in long prismatic needles, closely resembling ammonium chloride in appearance; the *platinichloride*—,

$$(C_4H_9NHCl)_2PtCl_4,$$

crystallises from water in glistening orange octahedra. The hydrochloride of tetramethyleneamine is converted by interaction with silver nitrite into *hydroxytetramethylene*,—

$$\begin{matrix}CH_2\cdot CH_2\\ |\quad\ |\\ CH_2\cdot CH(OH)\end{matrix},$$

which is a colourless oil boiling at 123°. On digestion with fuming bromhydric acid, hydroxytetramethylene is converted into a heavy oil, readily separable into two substances boiling at 105° and 174° respectively. The former is *bromotetramethylene*,—

$$\begin{matrix}CH_2\cdot CH_2\\ |\quad\ |\\ CH_2\cdot CHBr\end{matrix},$$

whilst the latter is a dibromobutane of the formula $C_4H_8Br_2$, which, however, is not identical with any of the known isomerides.

This result appears to show that, as in the case of trimethylene, the tetramethylene ring may under certain conditions be split by hydrogen bromide. These experiments are being extended to other derivatives of tetramethylene in order to obtain some clue to the course of the action.

129. "*β-2-Dimethylglutaric Acid*,—

$$(COOH\cdot CH_2\cdot C(CH_3)_2\cdot CH_2\cdot COOH.$$

By W. Goodwin and W. H. Perkin, jun., F.R.S.

Dimethylacrylic acid, $(CH_3)_2C{:}CH{\cdot}COOH$, is readily prepared by boiling methylic α-bromvalerianate,—

$$(CH_3)_2{\cdot}CH{\cdot}CHBr{\cdot}CO_2CH_3,$$

with alcoholic potash (compare Duvillier, *A. ch.*, [5], xix., 428); it crystallises from light petroleum in colourless needles which melt at 69°; when exposed to bromine vapour it is quantitatively converted into α-β-dibromvalerianic acid, $(CH_3)_2{\cdot}CBr{\cdot}CHBr{\cdot}CO_2H$, which melts at 108—110°.

Ethylic dimethylacrylate, $(CH_3)_2{\cdot}C{:}CH{\cdot}COOC_2H_5$ (b. p. 155°), when digested in alcoholic solution with ethylic sodio-malonate, is converted into ethylic dimethyl-propanetricarboxylate,—

$$EtCO_2{\cdot}CH{:}C(CH_3)_2+CH_2(CO_2Et)_2= =CO_2Et{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}CH(CO_2Et)_2.$$

This ethereal salt boils without decomposition at 203° (60 m.m.), and on hydrolysis yields the corresponding dimethylpropanetricarboxylic acid, which crystallises from water in colourless prisms melting at 175°. At 200° this acid is readily decomposed, evolving carbon dioxide and forming β_2-dimethylglutaric acid,—

$$COOH{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}CH(COOH)_2=CO_2+ +COOH{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}CH_2COOH.$$

This acid crystallises from water in plates, and melts at 100°; when digested with acetic anhydride it yields the anhydride—

$$CO{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}CO,$$
$$\underline{\qquad\qquad\qquad\qquad\qquad}$$
$$O$$

which melts at 124°.

β_2-Dimethylglutaric acid, therefore, like camphoric acid, with which it is probably closely allied, yields an anhydride, which melts at a higher temperature than the corresponding acid; the investigation of the products of the condensation of ethylic dimethylacrylate with homologues of ethylic malonate is in progress.

130. "*The Products of the Action of Fused Potash on Camphoric Acid.*" By A. W. CROSSLEY and W. H. PERKIN, jun., F.R.S.

Several years ago Hlasiwetz and Grabowsky (*Annalen*, cxlv., 205) studied the action of fused potash on camphoric acid, and stated that butyric acid, pimelic acid (isopropyl succinic acid), and an hydroxycamphoric acid, $C_{10}H_{16}O_5$, were obtained. As it seemed difficult to understand how butyric acid could be formed from camphoric acid, and as the authors were anxious to investigate the various hydroxycamphoric acids, they decided to carefully repeat these experiments.

They find that the fatty acids formed during the decomposition consist of large quantities of propionic acid and smaller quantities of at least four other fatty acids, among which are isobutyric acid, isovalerianic acid (?), and an acid of the formula $C_6H_{12}O_2$, boiling at 200°, which is probably isobutyl acetic acid, but no trace of butyric acid could be detected.

They have also failed to obtain any hydroxycamphoric acid; the acids of high boiling-point which we produced consist of large quantities of pimelic acid and small and varying quantities of unchanged camphoric acid.

It is hoped that the further investigation of this subject will give evidence of value in determining the constitution of camphoric acid.

131. "*Conversion of Ortho- into Para-, and of Para- into Ortho-Quinone Derivatives. II. Dinaphthyldiquinone.*" By S. C. HOOKER and J. C. WALSH, jun.

The authors have re-examined the supposed β-dihydroxydinaphthyldiquinone, which Kern (*Ber.*, xvii., 3019) obtained by oxidising the αα-dinaphthyldi-β-quinone discovered by Stenhouse and Groves. According to Kern, the product which is formed on exposing an alkaline solution of the quinone to the air is pale yellow; as, however, one of the authors had previously found that when β-naphthaquinone derivatives gave *pale* yellow products, still possessed of quinonoid properties, the change in colour involved a change of the β- into the α-naphthaquinone derivative, as it was improbable that an αα-dinaphthyldi-β-quinone could yield an α-dihydroxy-derivative, it appeared desirable to repeat Kern's experiments. The result has been the discovery that Kern's product is nothing more than the well-known β-hydroxy-α-naphthaquinone. The yield, however, is small, the larger portion of the diquinone being converted into a colourless compound or compounds soluble in water.

PHYSICAL SOCIETY.

Ordinary Meeting, April 13th, 1894.

Prof. A. W. RÜCKER, M.A., F.R.S., President, in the Chair.

MR. W. G. RHODES, M.Sc., was elected a member of the Society.

The PRESIDENT invited a Discussion on Prof. Henrici's paper "On Calculating Machines," and said a description of Mr. Sharp's Harmonic Analyser, giving direct readings of the amplitude and epoch of the various constituent simple harmonic terms, had been sent in.

This machine requires no adjustments to be made before using. The amplitude is given by the length of a line joining the initial and final portions of the point of contact of a roller with a rotating disc, whilst the epoch is determined by the angle which this line makes with the plane of the roller in its initial position.

Prof. PERRY congratulated Prof. Henrici on the success attained with his analysers. Referring to Planimeters, he said the average error made in working out indicator diagrams with Hine and Robertson's instrument was only about one-third that m[illegible] with Amsler's. After pointing out the great importance of Fourier's series to practical men, and especially to electrical engineers, he said that in studying reciprocating motions, such as those of pistons, valve gears, &c., it was most useful to resolve the motion into its fundamental harmonic motions and its overtones. In this way remarkable differences could be seen between various motions which have the same fundamental, and which are usually considered equivalent. In the *Electrician* of Feb. 5th, 1892, he had published the numerical work for a given periodic curve developed in Fourier's series, and he now exhibited a graphical solution done by one of his students, who was probably the first to carry out the late Prof. Clifford's idea of wrapping the curve round a cylinder and projecting it on different planes. Prof. Henrici had, he said, based the construction of his first analyser on Clifford's method, but used the Henrici principle (viz.,—

$$\int y \sin\theta\, d\theta = \int \cos\theta\, dy,$$

when integrated over a complete period) to explain the later machines. As a matter of fact, the first machine, in which the coefficients were determined by the Amsler planimeter carried by a reciprocating tangent plane, was a beautiful example of the Henrici principle, and he, Prof. Perry, saw great possibilities before it. The defects in the first instrument were mechanical, and could be got over by increasing the amplitude of the harmonic motion. Not only was the machine useful for Fourier expansions, but by giving suitable motions to the tangent plane developments of arbitrary functions in spherical harmonics, Bessel's functions, Lame's functions, and other normal forms could be determined. He had designed a machine which, on Prof. Henrici's principle, develops arbitrary functions in Bessel's, and hoped to have shown it in working order at the meeting; the Easter holidays had prevented its being finished in time. In this machine the motion is given to the table by a cam and roller, the cam being shaped so that the displacement of the table is $x \times J(x)$

when the shaft turns through an angle proportional to x. The revolving cylinder is driven by variable gearing from the cam shaft. By using curves of other shapes, developments in many normal forms may be obtained; the machine is therefore of general analytical use. An example of development in Bessels worked out arithmetically by two of his students, Messrs. Hunt and Fennel, was given, and the process of performing the integrations by the machine described.

Prof. Boys, speaking of arithmometers, said Prof. Selling's machine had several inconveniences. In the first place, it occupied a large space, and the projecting racks were apt to upset things just behind the machine. Secondly, the result of any operation was indicated by continuous motion, and therefore cannot be read off instantly with certainty. On the other hand, the "Brunsviga" machine was very compact and convenient, the only serious defect being that one cannot carry on figures obtained as the result of one operation to work with again, as was possible in the well-known Colmer machine. As another improvement, he suggested that the two sets of numbers on the wheels showing the result of any operation should be coloured differently, so that it would be easy to see whether multiplication or division had been performed. The labour of operating with large digits could then be considerably reduced with certainty. For example, in multiplying by 2998, instead of 28 (2+9+9+8) turns of the handle, 5 would be sufficient, viz., three in the forward direction and two backward, thus giving 3002. In his opinion logarithm tables were not nearly so convenient for ordinary calculations as this machine.

Mr. A. P. Trotter described how by the use of templates cut to suitable shapes one could obtain true curves from those given by recording voltmeters and similar apparatus.

Mr. Yule said he had recently seen the newest analyser made by Coradi for Prof. Weber, and was present when it was tested by the latter on a simple harmonic curve. It gave excellent results, the errors not amounting to 1 part in 2000. Speaking of the "hatchet" planimeter, he thought that the first one was exhibited by Mr. Goodman at the Institution of Civil Engineers.

Mr. A Sharp remarked that since last meeting he had designed an inversion of the mechanism in his harmonic analyser, which made it much more practical.

Prof. Henrici, in reply, said the uses of his first machine suggested by Prof. Perry might lead to great developments in this subject. Lord Kelvin had shown that with the sphere and roller integrator, products of two functions, such as $f(x)\,F(x)dx$ could be got. Referring to Prof. Boys' criticism on the Selling arithmometer, he did not consider the difficulty in reading off the result at all serious. Mr. Trotter's method of solving problems by templates might be very useful. Speaking of the "hatchet" planimeter, he said he believed it was first brought out in Denmark; Mr. F. W. Hill, of the City of London School, had sent him a solution of its action. Mr. Sharp, he said, had made a very considerable improvement in his machine, and the elements of this integrator may be useful for other purposes.

Mr. P. L. Gray, B.Sc., A.R.C.S., read a paper "*On the Minimum Temperature of Visibility*," describing experiments made to find the lowest temperature at which bright or blackened platinum becomes visible in the dark. The instrument used was a Wilson and Gray's modification of Joly's meldometer, in which a thin strip of platinum about 10 c.m. long and 1 c.m. wide is heated by an electric current. The expansion of the strip is indicated by an optical method and used for estimating the temperature of the strip. To calibrate the arrangement, small particles of substances having known melting-points were placed on the strip and observed through a microscope, the position of the spot of light showing the expansion being noted when the substance melted. The general conclusions arrived at are:—

1. That the minimum temperature of visibility is the same for a bright polished surface as for one covered with lampblack, although the intensity of radiation in the two cases may be different.

2. That the visible limit at the red end of the spectrum varies greatly for a normal eye, according to its state of preparation. Exposure to bright light diminishes the sensitiveness of the eye, and darkness increases it.

3. That for the less sensitive condition, the minimum temperature of visibility for the surface of a solid is about 470° C., but this may be much reduced by even a few minutes in a dark room.

4. That at night a surface at 410° C. is visible, and that by resting the eye in complete darkness this may be reduced to 370°, nearly.

5. That different people's eyes differ somewhat in their "minimum temperature of visibility," but probably not to any great extent if tested under the same conditions as to preparation, &c.

To most observers the strip at these low temperatures had no appearance of red, but looked like a whitish mist. Inserting a plate of glass or a layer of water in the line of vision had no effect on the temperature of visibility.

Mr. Blakesley enquired if the author had tried condensing the light from the strip. As to colourlessness, he observed that the parts of the retina active in oblique vision were less sensitive to colour than the central portions.

Dr. Burton remarked that in the experiments, the presence of light and not colour was being observed. When illumination was faint, as in twilight or moonlight, it was very difficult to distinguish colours. In the solar spectrum one did not see any whitish termination at the red end.

Mr. Elder said that Captain Abney had shown that all colours appear grey when of small intensity.

The President thought the question as to whether visibility depends on wave-length or on energy was an important one; probably a minimum amount of energy was essential. At such low temperatures the emission curves of the different wave-lengths may not have become sufficiently separated to be distinguished.

Mr. Gray, in reply, said Prof. Langley had shown that a minimum, but very small, amount of energy was necessary to vision in all parts of the spectrum.

Dr. Burton's paper on "The Mechanism of Electrical Conduction" was postponed.

OBITUARY.

JEAN CHARLES GALISSARD DE MARIGNAC.

On the 15th of this month the scientific world sustained a shock by the death of the illustrious chemist Jean Charles Galissard de Marignac in the seventy-sixth year of his life. The deceased was an Emeritus Professor of the University of Geneva, a Foreign Associate of the Royal Society of London, a corresponding Member of the Academy of Sciences of France, a Member of the Chemical Societies of London and Berlin, of the Royal Societies of Sciences of Sweden and of Prussia, and of the Royal Academy dei Lincei of Rome, of the Academy of Sciences at Turin, of the Royal Society of Upsala, of the Societies of Halle, Göttingen, Cherbourg, Basle, and Lausanne. The deceased chemist was, during the greater part of his long life, an indefatigable and successful worker in chemistry. Much of his attention was given to the recognition and the separation of that peculiar and intricate group of substances known as the rare earths. He studied the separation of the niobic and titanic acids, the compounds of niobium and of tantalum, the fluorides of antimony and arsenic, the fluoborates, the substances accompanying yttria. A number of his memoirs on these and kindred subjects will be found in the Chemical News. One of De Marignac's

most interesting memoirs is his critique on the work of Stas concerning the atomic weights. Whilst by no means rejecting the numbers arrived at by the Belgian chemist, he does not accept the conclusions drawn by the latter, or consider that they justify a renunciation of the hypothesis of Prout. He points out the number of elements which approximate very closely to the weights demanded by Prout, and suggests that if the numbers found do not exactly agree with the theoretical values, the difficulty may be occasioned by some "residual phenomenon" as yet undetected.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 15, April 9, 1894.

Spectra of Oxygen Raised to High Temperatures. Electric Method for Heating Gases.—J. Janssen.—This paper will be inserted in full.

Certain Novel Articles of Copper Derived from Ancient Egypt.—M. Berthelot.—The authors considers that an age of pure copper very probably existed before that of bronze. He regrets that historians and archeologists apply the term bronze indiscriminately to alloys and to pure copper. A copper vessel examined was deeply saturated with oxychloride produced by the prolonged action of brackish waters. It contained 71·9 per cent of copper, but neither tin, lead, antimony, zinc, or iron in appreciable proportions. A ring accompanying the vessel is formed of a plumbiferous bronze.

Slow Changes in Objects of Copper both Buried in the Earth and Preserved in Museums.—M. Berthelot.—The alterations are due to the initial presence of sodium chloride and of atacamite, whilst a proportion of metallic copper equal to that which was present in the atacamite in the state of cupric oxide passes into the cuprous state. All these reactions are exothermic. We have a cycle of reactions indefinitely recurring which destroys metallic copper buried in moist earth, and converts it into cuprous oxide.

Fusibility of Mixtures of Salts.—H. Le Chatelier.—The author studies the fusibility of mixtures of salts capable of combining so as to form double salts. These mixtures correspond to the aqueous solutions of salts which form hydrates. Two salts which form together a single definite combination will have a curve of fusibility composed of three distinct branches, the one corresponding to the crystallisation of one of the salts, the second to that of the other simple salt, and the third to that of the double salt. The author's results are shown in the form of a diagram.

Combination of Molybdenum Bioxide and Bisulphide with the Alkaline Cyanides.—E. Péchard.—The bioxide of molybdenum dissolves very readily in a solution of potassium cyanide, which then becomes very dense. The liquid is of a fine blue, and on concentration deposits blue crystalline needles of MoO_2Cy_2+2KCy. The solution, if treated with a dilute acid, takes a brown colour. Concentrated acids decompose it with an escape of hydrocyanic acid and the formation of a brown gelatinous precipitate. The blue solution of the double cyanide yields with the salts of the heavy metals characteristic precipitates. That with salts of lead is bluish white, with salts of copper a light brown, a greenish blue with mercuric salts, and a deep brown with the salts of silver. Recently prepared molybdenum bisulphide dissolves in a hot solution of potassium cyanide. The solution is of a deep green, and on cooling deposits a black mass of fine crystalline needles. The green solution gives a green precipitate with lead salts, a red precipitate with silver salts, and a brown with copper salts.

Use of Polishing in the Study of the Structure of Metals.—M. Osmond.—The author polishes with powders which are softer than the softest of the constituents of the metal, such as barium and calcium sulphates as obtained by precipitation. There is thus obtained a double indication—at first the production of hollows or of reliefs, and then the order of appearance of these hollows or these reliefs. It is easy under the microscope to distinguish a relief from a cavity by the following artifice:—The object lens is fixed at first a little below the focus and gradually raised. The reliefs which appear at first brilliant on a dark back-ground become by degrees dark on a brilliant ground. The hollows present inverse appearances. The author has studied the appearance of steels tempered at different heats, *e.g.*, at 1000°, at 770°, and at 670°.

Action of Halogens on Homopyrocatechine.—H. Cousin.—The action of chlorine upon homopyrocatechine has yielded trichlorohomopyrocatechine, the orthoquinone of the above body, and more highly chlorinised bodies, the study of which is incomplete. The action of bromine is analogous. Iodo-derivatives have not been obtained.

Revue Universelle des Mines et de la Metallurgie. Series 3, Vol. xxv., No. 2, February, 1894.

Electrolytic Separation of Chlorine and of Soda.—The method of Cross and Bevan has been derived from Lessueur's process for the electric treatment of common salt. At an establishment for the daily treatment of eighteen tons of salt the total expenses are 4000 francs, showing a daily profit of 2000 francs. This result is open to doubts.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 98.

Report made by H. Le Chatelier, on behalf of the Committee of Chemical Arts, on the Researches of Prof. Roberts-Austen.—An able and appreciative summary of the researches of Prof. Roberts-Austen on the alloys of silver, of gold, and on steel. The Committee addresses its congratulations to Prof. Roberts-Austen on his important researches on metallic alloys.

MISCELLANEOUS.

Royal Institution.—On Thursday, May 3, Professor Dewar will deliver the first of a course of lectures at the Royal Institution on "The Solid and Liquid States of Matter"; on Saturday, May 5, Captain Abney delivers the first of the Tyndall lectures on "Colour Vision"; and on Tuesday, May 1, Professor Judd begins a course of lectures on "Rubies."

Concerning the Absorption of Light in Platinum at Various Temperatures.—G. B. Rizzo.—The author's results establish a new correlation between electricity and light. As the electric resistance of a conductor increases with the increase of its temperature, its transparence for light increases also. In diaphanous bodies with the rise of temperature the electric resistance declines and the transparence decreases.—*Il Nuovo Cimento*, Jan., 1894.

New Publication.—The first number of a new publication, specially intended as the organ of electrochemists and electro-metallurgists, &c., has just seen the light in Berlin. The new journal, which is called the *Electrochemische Zeitschrift*, is to be published monthly, and is edited by Dr. A. Neuburger. The list of contributors is an influential one, comprising as it does such names as Prof. Slaby, Prof. Dürre, Prof. Ostwald, Prof. Aron, Prof. Goppelsroeder, and many others.

MEETINGS FOR THE WEEK.

MONDAY, 30th.—Society of Arts, 8. (Cantor Lectures). "Typewriting Machines," by Henry Charles Jenkins, A.M.Inst.C.E.
—— Medical, 8.30.
TUESDAY, May 1st.—Royal Institution, 3. "Rubies—their Nature, Origin, and Metamorphoses," by Prof. J. W. Judd, F.R.S.
—— Institute of Civil Engineers, 8.
—— Pathological, 8.30.
WEDNESDAY, 2nd.—Society of Arts, 8. "Nickel," by A. G. Charleton, A.R.S.M.
THURSDAY, 3rd.—Chemical, 8. Ballot for the Election of Fellows. "The Structure and Chemistry of the Cyanogen Flame," by Prof. Smithells. "The Condition in which Carbon Exists in Steel," by J. O. Arnold. "α-Hydrindone and its Derivatives," by Dr. Kipping. "Volatile Compounds of Lead Sulphide," by J. B. Hannay.
—— Royal Institution, 3. "The Solid and Liquid States of Matter," by Prof. Dewar, F.R.S.
FRIDAY, 4th.—Royal Institution, 9. "Sound Production of the Lower Animals," by Professor Charles Stewart, Pres.L.S.
—— Quekett Club, 8.
—— Geologists' Association, 8.
SATURDAY, 5th.—Royal Institution, 3. (The Tyndall Lectures). "On Colour Vision," by Capt. Abney, F.R.S.

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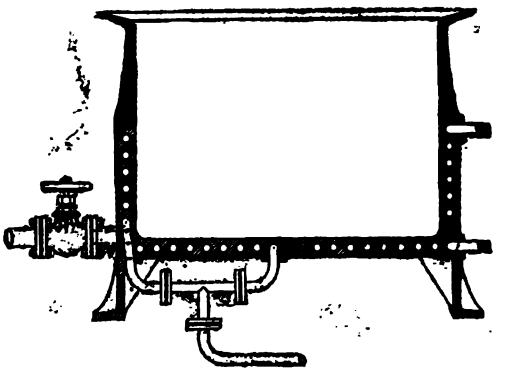

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says;—
P. 316. "An improved vessel for boiling oil, and suitable for many other kindred purposes, has been recently described by T. Frederking (CHEMICAL NEWS, London). A coil of stout piping is arranged in a casting mould, so that the molten metal forming the pan is cast round the coil, much as is done in the case of the water-tuyeres of a blast furnace. Steam at any pressure [or any other heating medium] being passed through the coil, the pan is heated up proportionately without any danger, the pressure bearing solely on the piping and not on the metal pan itself, whilst the well conducting metal walls allow the heat to pass readily. Temperatures up to 350° and 400° C. can be thus obtained."
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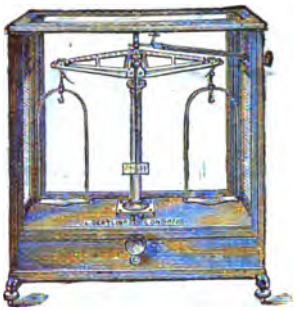

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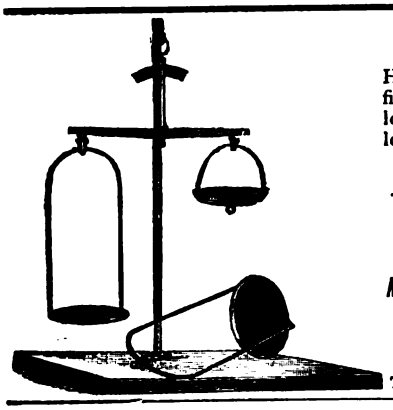

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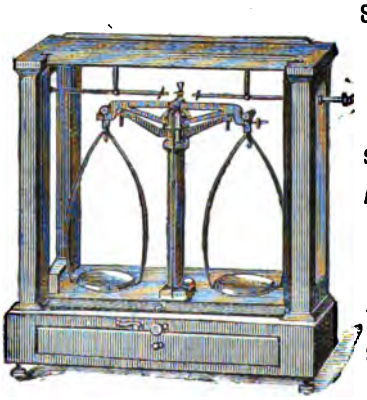

FIG. 3a.

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THE CHEMICAL NEWS.

Vol. LXIX., No. 1797.

ON THE NATURE OF NITROGEN.

By Dr. T. L. PHIPSON,
Formerly of the University of Brussels, and the Laboratoire de Chimie Pratique, Paris, &c.

During the course of last year I published some experiments and observations concerning the chemical constitution of atmospheric air, the origin of its oxygen, and the anaërobic character of plants. From these researches there results a new theory of the earth's atmosphere, and a new light is thrown on the functions of the vegetable world. I may indicate the propositions briefly thus:—

1. During the period of gaseous existence the heat was so intense that no compounds could exist.

2. As the surface of the globe cooled, and compounds became possible, nitrogen alone, on account of its neutral nature, formed the primitive atmosphere of the earth.

3. Before the advent of life, carbonic acid was abundantly diffused into this primitive atmosphere by volcanic action, and it was saturated with vapour at the temperature it then had; but it contained no free oxygen, for we find oxidisable substances in the primitive rocks.

4. In this atmosphere of nitrogen, carbonic acid, and vapour, *anaërobic*, or *plant life*, made its appearance under the mysterious agency of the sun's light, and from that period free oxygen began to be diffused into the atmosphere.

5. In the course of ages the quantity of free oxygen thus produced, gradually increasing, the anaërobic cells underwent the influence of a change of medium and *aërobic* or *animal life* gradually appeared.

6. The quantity of oxygen in the air has gone on increasing ever since, and its present *maximum* coincides with the highest development yet attained of the animal nervous system.

7. The plants of our present period are still essentially of an anaërobic nature, as were those of the primitive geological periods.

The inert nature of the nitrogen which caused it to form the primitive atmosphere of our globe has proved a source of uncertainty in the minds of the ablest chemists, more especially Berzelius and Graham. Several chemists have imagined it must be a compound and not an element; and attempts have been made to decompose it. Attention has been called to the fact that it unites with oxygen to form one of the most powerful *acids*, and with hydrogen to form one of the most powerful *alkalis*. Now, as Berzelius remarked, other elements combine both with oxygen and with hydrogen, but always to form acids. It is true that phosphorus and arsenic resemble nitrogen to a certain extent in this respect, but they form nothing comparable with *nitric acid* and *ammonia*.

Berzelius was not fully aware of the essentially neutral nature of nitrogen which caused it to form the primitive atmosphere of the earth. It is the *only element* of this essentially inert nature; so that in nitric acid it does not at all mask the electro-negative properties of oxygen, nor in ammonia the electro-positive properties of hydrogen; but he knew that "bodies which burn at the expense of nitric acid or of nitrates develop a temperature almost as high as when they burn in pure oxygen."

At the present day nitrogen still forms no less than about four-fifths of our atmosphere, and is not found in the crust of the earth, save in comparatively small quantities, as a component of certain substances (nitrates, urates, ammonia), which are undoubtedly the *residues of organic life*.

In plants and animals nitrogen is present in greater proportion than in the rocky strata of the globe; for plants and animals have been formed from the atmosphere and its re-union with the mineral elements of the earth, under the mysterious influence of the sun's light.

The Casa Mia Laboratory, Putney,
London, S.W., May 1st, 1894.

THE PURIFICATION OF WATERS FOR FEEDING STEAM-BOILERS.

By Dr. R. JONES.

In order to ascertain whether a sufficient quantity of alkali has been added for precipitating the alkaline earths, the author recommends the following procedure:—

(*a*) If the water, after ebullition, has not an alkaline reaction he takes 10 c.c. of the water from the boiler, cooled and filtered, and adds 2 drops of an alcoholic solution of phenolphthalein (2 parts in 1000 alcohol).

1. The water remains colourless. The addition of alkali has been insufficient, and must be increased.

2. The water turns red, but is decolourised by two drops of semi-normal hydrochloric acid. The water is normal.

3. The water is reddened and retains the colour after the addition of two drops of semi-normal hydrochloric acid.

The quantity of alkali added is too great and must be diminished.

(*b*) The water has an alkaline reaction after boiling.

In this case 20 c.c. of the filtered water are mixed with four drops of a solution of calcium chloride (1 : 20).

There appears an abundant precipitate of calcium chloride, which does not disappear on the addition of four drops of semi-normal hydrochloric acid. The addition of alkali has been excessive and must be reduced.

2. There appears after a short time only a few flocks, which re-dissolve on the addition of four drops of semi-normal acid. The water is normal.

3. There appears no precipitate.

We take a fresh sample of the filtered water, add five drops of a solution of soda (1 : 5) and allow it to stand for one hour. If the water still remains clear it is normal, but if a precipitate appears more soda must be added to the water which has to be purified.—*Zeit. für Angewandte Chemie.*

ON THE SPECTRA OF OXYGEN RAISED TO HIGH TEMPERATURES: ELECTRIC METHOD FOR HEATING GASES.

By J. JANSSEN.

The question of the presence of oxygen in the gaseous coatings of the sun presents distinct cases.

Firstly, that in which oxygen gas might be found in the external parts of the coronal atmosphere, *i.e.*, in a medium where the temperature may approach the temperatures of the terrestrial atmosphere.

In this case the spectral manifestations of this gas would be similar to those which it presents in the earth's atmosphere. To prove its absence in these parts of the coronal atmosphere it is sufficient to show that the rays and bands due to this body in the sun's atmosphere are produced totally in number and intensity by the earth's atmosphere. It is known that this point has been the subject of my three ascents of Mont Blanc, and of special experiments at the observatory of Meudon.

But the case which regards ordinary temperatures

represents only one part of the question. Oxygen which should exist in the mean and in the lower parts of the coronal atmosphere, in the chromosphere, and in the photosphere would be raised to higher and higher temperatures, and to decide by means of spectral analysis on its presence in these regions it is, above all, necessary to know the modifications which a rise of temperature may produce in the spectral manifestations of oxygen.

I have occupied myself with this phase of the question almost at the outset of my studies, and even before commencing my ascents of Mont Blanc.

This study presents especial difficulties. The rays and bands of O require for their production very thick layers of this gas. The Group B especially is merely nascent in the spectrum of a pencil of rays which has traversed a thickness of 60 metres of this gas at a pressure of two atmospheres.

The dark band situate near the ray D, and which is the first to manifest itself, requires with the above thickness of 60 metres a pressure of six atmospheres. We conceive the difficulty of heating similar gaseous columns to high temperatures. We may, indeed, reduce the thickness of these columns by increasing the pressure, but then the tightness of the joints is endangered by the heat which they would have to support.

To overcome this difficulty I have concluded to have recourse to electricity.

By a special arrangement of the use of this agent, I have been able to heat a gaseous column to incandescence without appreciably heating the tube containing the gas, and consequently leaving the joints uninjured.

The following is the arrangement adopted:—

A tube of steel, 2·20 metres in length and 6 c.m. in diameter was bored so as to make an internal channel of 3 c.m. in diameter. This tube, which could resist internal pressures of more than 1000 atmospheres, is closed at its ends by screw pieces bearing sights of glass or quartz, permitting the passage of light into the axis of the tube. A steel cock permits the introduction of the gas at the desired pressure.

The rise of temperature is obtained by means of a spiral formed by a platinum wire of a thickness suitable to its length and to the power of the electric source which has to raise the gas to the temperature required. This spiral traverses the whole internal channel, and the wire of which it is formed issues at its ends. It is electrically insulated from the steel by means of a jacket of asbestos, which opposes the transmission of the heat of the spiral to the sides of the tube. At the ends of the spiral the wire penetrates into a small channel, of the same diameter, bored in a thick copper wire, forming an end-piece which traverses the wall of the tube without electrical contact, and puts the wire of the spiral in communication with the source of electricity. This end-piece, of a cylindrical form, is slightly extended in its lower part at the point where it receives the wire of the spiral.

The insulation of the end-piece is obtained by means of a ring of ivory or compressed fibres strongly fixed between the end-piece and the tube. This fixation is effected by means of a nut screwed into the wall of the tube and acting upon the upper surface of the ring without contact with the stop of copper. On the other hand, by another nut screwed upon the stop, but insulated from the tube by a disc of an insulating substance. The ring is thus found engaged in a space which is contracted at pleasure, and consequently exerts upon it a compression in proportion the effort of the gas within which has to be resisted.

By this arrangement, and by means of suitable external resistances, we may raise the spiral to the heat desired from the ordinary temperature to white-redness, and communicate these temperatures to the gaseous column without appreciably heating the sides of the steel tube.

As for the closures of the ends, they are obtained in the ordinary manner with pieces of glass or of quartz. I will say merely that we usually line the glasses by placing within or at the side where the heat is most felt the thinnest glass, which is least liable to break under the influence of changes of temperature. This arrangement of double glasses is important; it avoids the danger which might result from the rupture of a glass and the projection of its fragments. We use it in all our experiments, even if working only at ordinary temperatures.

I will add, as a working detail, that to fill the space between the glass ends and the extremity of the spiral we place glasses of the internal diameter of the tube.

The luminous sources employed are the arc light, the Drummond, or, in certain cases, that of the sun. The pencil of rays must be rendered parallel before entering the tube and concentrated on issuing from the slit of the spectroscope by means of convex or cylindrical lenses.

We have been led to experiment on giving the tube a vertical position.

The eddies and movements of the gaseous column under the action of the spiral heated to whiteness often diminish the transmission of light to an enormous extent. In the vertical position all the gaseous strata are brought to arrange themselves horizontally, and are attacked normally by the rays which increase in a considerable and unexpected manner the quantity of light transmitted. In this case the optical study of the pencil of rays is brought to ordinary conditions by means of totally reflective prisms.

The results obtained with oxygen will be described in a future communication.—*Comptes Rendus.*

REPORT OF COMMITTEE ON DETERMINATIONS OF ATOMIC WEIGHT PUBLISHED DURING 1893.*

By F. W. CLARKE.

(Concluded from p. 197).

Miscellaneous Notes.

Richards and Rogers, in a paper upon the occlusion of gases by metallic oxides (*Proceedings of the American Academy*, xxviii., 200; presented May 10, 1893), show that when the oxides of copper, nickel, zinc, and magnesium are prepared by the ignition of the nitrates, they retain appreciable quantities of gaseous impurities, such as nitrogen and oxygen, especially the former. The oxides of cadmium, mercury, lead, and bismuth, similarly prepared, contained no gaseous occlusion, excepting a mere trace in the case of cadmium. This observation reveals a possible serious source of error in several determinations of atomic weight, particularly in the cases of zinc and magnesium. In consequence of this fact, the atomic weight of zinc is now under re-investigation in the Harvard laboratory, the compounds selected for study being the chloride and bromide.

In the study of the rare earths, rough determinations of atomic weight are of great importance in the identification of material. Commonly they are made by the sulphate method, which is familiar to all chemists. Gibbs (*Am. Chem. Journ.*, xv., 546, Nov., 1893), however, in a study of these substances, makes use of the oxalates. By ignition, the oxide is left and can be weighed, while the proportion of oxalic acid is easily determinable by titration with permanganate solution. In some cases the oxalates were ignited with weighed quantities of pure sodium tungstate, the increase in weight representing R_2O_3. From the ratio between R_2O_3 and C_2O_3 the molecular weight of the oxide is easily calculated, and agrees well with determinations made by the sulphate process. Hinrichs, in a series of communications published in the *Comptes Rendus*,† attempts to show that Stas's determinations of atomic weights are vitiated by systematic errors, depend-

* From the *Journal of the American Chemical Society*, xvi., No. 3.

† On the $KClO_3$ work, in cxv., 1074; on the lead determinations, in cxvi., 431.

ing upon the quantities of material weighed. According to him the larger the weight of the substance employed the larger the error; and he constructs curves to represent his views graphically. His mathematical procedure, however, his "method of limits," is not clear, and it savours somewhat of assuming Proutian values in advance, and then regarding variations from them as errors for which corrections should be applied. At all events he fails to point out, on the basis of experimental evidence, how the supposed errors were produced, and he does not show that they could have been of sufficient magnitude to account for the divergences to be explained. If Stas's work is to be set aside, it can be by experimental researches only.

In a third paper (*Comptes Rendus*, cxvi., 695), the same author gives his mathematical process in some detail, and still later he discusses Dumas's experiments relative to the atomic weight of oxygen (*Comptes Rendus*, cxvi., 753), seeking to show that it is exactly 16. Very recently he has also discussed the determinations of the same constant made by Keiser, Cooke and Richards, Morley, and Dittmar and Henderson, reaching the conclusion that the ratio H : O = 1 : 16 rigorously (*Comptes Rendus*, cxvii., 663). He objects especially to the use of averages as fallacious, but does not fully establish the legitimacy of his conclusions.

In another journal (CHEM. NEWS. lxviii., 171, Oct. 6, 1893), Hinrichs criticises Richards's researches upon the atomic weight of copper. After showing that several published determinations of the electrolytic ratio between silver and copper agree quite well with the ratio 108 : 63·5, he takes up in particular Richard's analyses of copper sulphate, and points out that a part of the data correspond with the even values O = 16, S = 32, and Cu = 63·5. The other work of Richards he dismisses as erroneous, but neglects to show wherein the errors lie.

In still another paper (*Comptes Rendus*, cxvii., 1075), Hinrichs proposes to abandon gases like O and H as bases for atomic weight determinations, and to adopt carbon (diamond) = 12 as the fundamental standard, on the ground that it can be exactly weighed. Oxygen and calcium are combined with this as sub-standards, becoming 16 and 40 respectively.

Replies to Hinrichs's criticism of Stas have been published by Spring (*Chem. Zeit.*, xvii., 242, Feb. 22, 1893) and by Van der Plaats (*Comptes Rendus*, cxvi., 1362). Both writers object to the processes of extrapolation of which Hinrichs makes use, and Van der Plaats shows by tabulation of data that the systematic errors alleged to exist in Stas's experiments are not there. Only fortuitous errors occur, and these are of insignificant magnitude. Furthermore, the ratios determined by Stas are so numerous, so varied, and so concordant in their final results that the presumption in their favour is overwhelming.

In the same paper, indeed, as its main object, Van der Plaats gives the results of a re-calculation of Stas's twenty-one ratios by the method of least squares. He does not, however, give his equations nor explain the

	A.	B.
Ag	107·9244 ± 0·0136	107·9202
Cl	35·4565 ± 0·0049	35·4516
Br	79·9548 ± 0·0101	79·9497
I	126·8494 ± 0·0166	126·8445
S	32·0590 ± 0·0085	32·0576
K	39·1403 ± 0·0059	39·1414
Na	23·0443 ± 0·0043	23·0453
Li	7·0235 ± 0·0051	7·0273
Pb	206·9308 ± 0·0404	206·9089
N	14·0519 ± 0·0078	14·0421
NH_4.. ..	18·0740 ± 0·0034	18·0760
Hence H =	1·0055 ± 0·0021	1·0085

TABLE OF ATOMIC WEIGHTS, REVISED TO JAN. 1, 1894.

Name.	Atomic weight.
Aluminium	27·
Antimony	120·
Arsenic	75·
Barium	137·43
Bismuth	208·9
Boron	11·
Bromine	79·95
Cadmium	112·
Cæsium	132·9
Calcium	40·
Carbon	12·
Cerium	140·2
Chlorine	35·45
Chromium	52·1
Cobalt	59·
Columbium	94·
Copper	63·6
Erbium	166·3
Fluorine	19·
Gadolinium	156·1
Gallium	69·
Germanium	72·3
Glucinum	9·
Gold	197·3
Hydrogen	1·008
Indium	113·7
Iodine	126·85
Iridium	193·1
Iron	56·
Lanthanum	138·2
Lead	206·95
Lithium	7·02
Magnesium	24·3
Manganese	55·
Mercury	200·
Molybdenum	96·
Neodymium	140·5
Nickel	58·7
Nitrogen	14·03
Osmium	190·8
Oxygen	16·
Palladium	106·6
Phosphorus	31·
Platinum	195·
Potassium	39·11
Praseodymium	143·5
Rhodium	103·
Rubidium	85·5
Ruthenium	101·6
Samarium	150·
Scandium	44·
Selenium	79·
Silicon	28·4
Silver	107·92
Sodium	23·05
Strontium	87·6
Sulphur	32·06
Tantalum	182·6
Tellurium	125·
Terbium	160·
Thallium	204·18
Thorium	232·6
Thulium	170·7
Tin	119·
Titanium	48·
Tungsten	184·
Uranium	239·6
Vanadium	51·4
Ytterbium	173·
Yttrium	89·1
Zinc	65·3
Zirconium	90·6

special form of the method which he used. The results are stated in two tables—one (A) computed upon the supposition that each ratio is entitled to weight inversely proportional to the square of its mean error; the other (B) regarding all as of equal weight. O=16 is the base of the system.

Another contribution to the Hinrichsian literature is furnished by E. Vogel (*Bull. Acad. Bruxelles*, (3), xxvi., 469), who criticises Stas at considerable length. His paper is preceded by adverse reports from W. Spring and L. Henry.

In conclusion I submit a Table of Atomic Weights revised to January 1, 1894. Oxygen =16 is taken as the base of the system, but for provisional reasons only. Before long, with improved determinations, it may be practicable to return to the more philosophical H=1, when the entire system can be transformed once for all into something like permanent shape. A premature transformation of this kind, however, would only work confusion, without corresponding benefit.

EXPERT TESTIMONY.*

By WM. P. MASON.

A NUMBER of years ago several very able articles appeared in *Nature*, upon the subject of Expert Testimony, showing how desirable it is to have the scientific witness removed as far as possible from the position of a partisan, and suggesting that such an end could be best obtained by having the experts employed by the bench rather than by the bar. Some recent experiences of my own, which I beg permission to recount, call to my mind those *Nature* articles very forcibly. A poison case in which I was lately employed may be roughly outlined as follows:—

Much arsenic and a very little zinc were found in the stomach.

The body had not been embalmed, but cloths wrung out in an embalming fluid containing zinc and arsenic had been spread upon the face and chest.

Medical testimony showed that no fluid could have run down the throat. Knowing the relative proportions of zinc and arsenic in the embalming fluid, the quantity of arsenic found in the stomach was twelve times larger than it should have been to have balanced the zinc also there present, assuming them to have both come from the introduction of the said embalming fluid by cadaveric imbibition. Other circumstantial evidence was greatly against the prisoner.

At the time of my appearing for the people, on the occasion of the first trial of the case, my direct testimony brought out very strongly the fact of a fatal quantity of arsenic having been found in the stomach, but no opportunity was given me to testify to the presence of the zinc found there as well, although the fact of its existence in the body was known to the prosecution through my preliminary report. Through ignorance of the nature of such report on the part of the defence, no change was made in the character of my testimony during the cross-examination, and I was permitted to leave the witness stand with a portion of my story untold. No witnesses were called for the defence, and the case was given to the jury with the darkest of prospects for the prisoner.

For many reasons, unnecessary to recount here, I was distinctly of the opinion that murder had been committed, but I felt, nevertheless, that common justice demanded that the prisoner should have been entitled to whatever doubt could have been thrown upon the minds of the jury, no matter how far-fetched the foundations for such doubt might have been.

The first trial having resulted in a disagreement of the jury I was pleased to learn, before the second hearing of the case began, that the defence was prepared to go into the question of the embalming fluid, for the responsibility of permitting only a part of what I knew to be drawn from me, to the entire exclusion of the remaining portion, was greater than I wished to assume. The nature of my report to the coroner having been established, and certain opinions relating thereto having been fully ventilated, the jury were possessed of "reasonable doubt" and acquitted the prisoner. What now were the duties of the expert upon the occasion of the first trial of this case and how should he have constructed the meaning of his oath?

One eminent legal light, to whom the question was referred, held that the expert was distinctly the property of the side employing him, and that his duty was simply to answer truthfully the questions put to him, without attempting to enlighten the court upon facts known to him, but not brought out by the examination, no matter how vital such facts might be.

Another held that although the above course would be proper in a civil case, yet in a matter involving life and death the witness should insist upon the court becoming acquainted with his whole story. Do not such differences in legal opinion make it yet more desirable that the expert, at least in capital cases, should be the employee of the bench, rather than of the bar, in order that whatever investigations are made may be entirely open to public knowledge and criticism.

* *Journal of the American Chemical Society*, xvi., No. 4. Read at the Baltimore meeting, December 28, 1893.

GOLD MOIRÉ-MÉTALLIQUE.*

By A. LIVERSIDGE, M.A., F.R.S.
Professor of Chemistry in the University of Sydney.

IN experimenting upon the reduction of gold from solution, to test the theories of the formation of gold nuggets, I found that the pure gold plates and foil which I used (which will be described in a future paper), in many cases presented a moiré-métallique appearance, such as is so familiar to us in tin plate and galvanised iron. The whole surface of the plate became dotted over with more or less regular crystals like those often seen on tin plate; they are, however, much more regular and rectangular in outline and very small, the majority being less than one m.m. square.

Afterwards I found that this crystallisation could be brought about by merely boiling the pure gold foil or plate in hydrochloric acid. The acid, although free from nitric acid, dissolved traces of the gold, probably due to a little free chlorine.

This moiré métallique gold may have been observed before, but I have not come across any reference to it. Advantage might be taken of it for decorative purposes on jewellery and other articles made of gold plate.

SEA WATER AS A CHEMICAL AND MECHANICAL DEPOLARISING AGENT FOR PRIMARY BATTERIES.

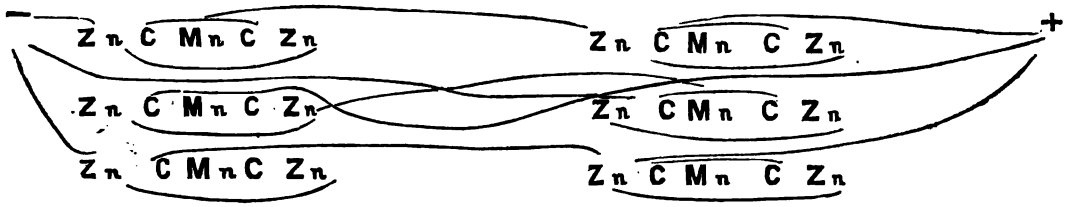
By P. L. ASLANOGLOU.

I HAVE recently had the opportunity of experimenting with primary batteries at a Mediterranean port, and there found that satisfactory results were obtainable when sea water was substituted for ammonium chloride in a Leclanché cell. I am not aware whether this has been observed before, but it occurred to me that the following suggestion might be of some interest.

* Read before the Royal Society of New South Wales, September 6, 1893.

Where the rise of the tide is comparatively small, a frame constructed of wood bearing a mixed series (as shown in the woodcut) might be suitably anchored; or I should suggest a breakwater of four walls with apertures at the bottom. This form of batteries are to swing on four pivots like a compass, and I venture to predict that the motion caused by the water will be quite sufficient to mechanically depolarise the plates.

On shallow coasts such as those in England the series



could be imbedded in the moist sand or shingle just below the high water mark, employing such material for fittings as would resist the action of salt water.

A battery as described above would be cheaper than the Leclanché when only small E.M.F. is required.

THE ATOMIC WEIGHT OF PALLADIUM.*

By EDWARD H. KEISER and MARY B. BREED.

(Concluded from p. 198).

Analysis of the Palladium Diammonium Chloride.

The ratio of palladium to palladammonium chloride was determined by reducing weighed quantities of the dried compound in a current of hydrogen. The palladammonium chloride was weighed in platinum boats. It was dried in an air-bath at a temperature of 110—120° until constant weight was obtained. The boat was then introduced into a combustion-tube through which a current of pure hydrogen was passed. The hydrogen was made by the action of pure dilute hydrochloric acid upon pure zinc, and was washed with alkaline lead solution and potassium permanganate. It was then dried by passing over solid caustic potash, after which it passed over red-hot metallic copper, and, finally, before entering the reduction tube, it was dried with phosphorus pentoxide. After the hydrogen had been passing through the reduction tube for some minutes, and all air had been expelled, the portion of the tube containing the boat was heated very gently. The palladammonium chloride unites with the hydrogen very gradually under these circumstances. There is no decrepitation whatsoever, and by gently raising the temperature the ammonium chloride slowly sublimes. The sublimate in all cases was found to be perfectly snow-white in appearance. *There was absolutely no loss of palladium by volatilisation nor by decrepitation,*† as was shown by a careful examination of the aqueous and acid washings of the tube after the reduction had been finished. In neither solution could a trace of palladium be found when tested with potassium iodide or with hydrogen sulphide. It is only when an imperfectly dried specimen of palladammonium chloride is heated very rapidly in a current of hydrogen that there is loss by spattering and the mechanical carrying away of minute particles of palladium.

The results of the analysis of the palladammonium chloride prepared from distilled palladium chloride are as follows :—

Number.	Weight of $PdN_2H_6Cl_2$ taken.	Weight of Pd obtained.	Atomic weight.
1	1·60842	0·80997	106·271
2	2·08295	1·04920	106·325
3	2·02440	1·01975	106·334
4	2·54810	1·28360	106·342
5	1·75505	0·88410	106·341
Total	10·01892	5·04662	[106·325]

Reducing now the weights in air to the weights in a vacuum, by adding the weight of air displaced, we obtain the ratio :—

$PdN_2H_6Cl_2 : Pd :: 10·02373 : 5·04717$ or $Pd = 106·246$.

In this calculation the specific gravity of palladium is taken as 11, and that of the palladium diammonium chloride as 2·5; values found as the result of duplicate determinations. The following atomic weights have been used :—H = 1, N = 14·01, Cl = 35·37. The weight of a cubic centimetre of air is taken as 0·0012 grm.

Purification of Palladium in the Wet Way.

In order to test the accuracy of the determinations made in 1889, we decided to purify some palladium by the method then used, with additional precautions. A piece of palladium foil, weighing about 15 grms. was therefore dissolved in aqua regia, and the solution of dichloride thus obtained evaporated to dryness. The residue was then dissolved in water, to which a little hydrochloric acid was added, and the filtered solution was treated with ammonia and warmed upon the water-bath until the precipitate first formed was dissolved. The insoluble residue, containing iron and other impurities, was filtered off; but the filtrate was pale bluish green in colour, owing to the presence of copper. Hydrochloric acid gas, made by allowing pure concentrated sulphuric acid to act on pure strong hydrochloric acid, and washed through a concentrated solution of hydrochloric acid, was passed into the solution. The palladium diammonium chloride thus precipitated was washed by decantation, and then upon the filter with the aid of a suction-pump, and afterwards redissolved in very dilute ammonia. This process of precipitating and dissolving the substance was repeated five times. All rhodium and the last trace of iron were thus removed; the bluish colour gradually disappeared from the ammoniacal solution, which became a clear straw colour, showing that all copper had been removed. The salt was then dried in desiccators, and the metal obtained from it by reduction in hydrogen, as before described.

The spongy metal was then again dissolved in aqua regia, evaporated repeatedly with hydrochloric acid to expel nitric acid, and the chloride dissolved in very dilute hydrochloric acid. In order to make sure that no gold was present, sulphur dioxide was passed into the solution. The gas was prepared from pure sulphuric acid and copper, was washed through water, and run into the solution of palladium until the colour changed from dark red to yellow. The solution was protected from dust and allowed to stand for a week, but no gold was found to be precipitated, and the solution was therefore evaporated to dryness to expel sulphur dioxide. The residue, after being dissolved in water containing hydrochloric acid, and treated with ammonia, was converted into palladammonium chloride in the same manner as before. At this point, however, it became evident that not only had the

* From the *American Chemical Journal*, xvi., No. 1.

† Keller and Smith (*Am. Chem. Journ.*, xiv., 423) found that palladium was volatilised. This was no doubt due to a rapid reduction of the imperfectly dried compound in a strong current of hydrogen. The metal used by one of us (K.) in the earlier determinations was not, as they suppose, obtained from Eimer and Amend in New York

introduction of sulphur dioxide been unnecessary for the purification of the substance, but had become itself a source of difficulty; for the palladammonium chloride was now dull brownish yellow, instead of pure orange-yellow as before. Dissolving and re-precipitating did not alter the appearance of the salt, and when dried it turned dark brown on all the surfaces exposed to the air. We decided that it would be necessary to reduce to the metallic form in order to expel sulphur. This was done in the same was as before, and the reduced metal was again converted into palladammonium chloride. Though the freshly precipitated salt was now of the proper colour, yet it changed as soon as it dried, becoming dull lemon-yellow throughout, and turning brown on the exposed surfaces. That the source of difficulty lay in some foreign substance present in the salt itself was shown by the fact that the change in colour took place when the most careful precautions were taken to exclude all laboratory fumes from the workroom, and when the salt was placed in the desiccator as soon as the washing was completed. After precipitating and re-dissolving the salt three times, but without removing the impurity, we reduced it again in a current of hydrogen, and then, placing the reduced metal in a hard glass tube, through which hydrogen was passing, heated it in the combustion furnace, and kept the metal at a bright red heat for five minutes. After cooling, it was dissolved again in aqua regia, evaporated repeatedly with hydrochloric acid, dissolved in water and a few drops of the acid, and the solution was then treated with mercuric cyanide in slight excess. The palladium cyanide thus precipitated was allowed to settle, and was washed by decantation repeatedly. It was then washed on the filter, dried in desiccators, and reduced to metallic form by heating in the air. Cyanogen gas was given off, and after the reaction was complete, the heating was continued for about an hour, to expel any mercury that might have been retained mechanically by the very gelatinous precipitate of palladium cyanide. The metal, which was partly oxidised, was reduced in a Rose crucible in a current of hydrogen, dissolved in aqua regia, the solution evaporated repeatedly with hydrochloric acid, and then digested with ammonia. Just as the precipitate thus formed was about all dissolved, a white crystalline precipitate separated in small quantity, which, when filtered off, proved to be the so-called "white precipitate" formed by the action of ammonia on mercuric chloride. The small quantity of mercury that could not be removed by heating was thus separated by filtration, and the palladium was then precipitated as palladammonium chloride by running in hydrochloric acid gas. The precipitate, after washing, was dissolved and re-precipitated, to prove that all mercury had been removed, washed, and dried for several months in a desiccator over solid caustic potash.

Analysis of Palladium Diammonium Chloride Purified by Precipitation.

The palladium in the salt was determined in the same way as in that purified by distillation—*i.e*, the substance was weighed out in platinum boats, dried to constant temperature, and reduced in a current of hydrogen prepared and purified in the manner before described. In these analyses, as in the others, the sublimate was in every case tested for palladium which might have been carried out of the boat, but no trace of the metal was found in the washings.

The results of the analysis of the palladium diammonium chloride prepared in the wet way are as follows :—

No.	Wt. of $Pd(NH_3Cl)_2$ taken.	Wt. of Pd found.	Atomic weight.
1	1·50275	0·75685	106·297
2	1·23672	0·62286	106·296
3	1·34470	0·67739	106·343
4	1·49059	0·75095	106·353
Total	5·57476	2·80805	[106·322]

Highest = 106·353
Lowest = 106·296
Difference = 0·057

Reducing the weights in air to the weights in vacuum by adding the weight of air displaced, we obtain the ratio :—

$PdN_2H_6Cl_2 : Pd :: 5·577436 : 2·808356$,
or atomic weight of Pd = 106·245.

The value found is practically the same as in the first series.

The earlier determinations of one of us have been criticised on the ground that sufficient precautions were not taken to ensure the purity of the palladammonium chloride that was analysed, and that in the reduction of this compound in a stream of hydrogen there was loss by decrepitation and the mechanical carrying away of metal by the hydrogen. In repeating the work we have met these objections by devising a new method for the purification of palladium compounds, namely, the fractional distillation of palladium chloride in a current of chlorine. We have purified palladium chloride in this way and converted it into palladammonium chloride. We have also prepared the latter compound by the best known methods in the wet way. We have analysed both specimens by reduction in pure hydrogen. We have shown that this was done without loss of metal. And as the result we get in each case for the atomic weight the value 106·25—a number that agrees very closely with the value first obtained, viz., 106·27. We propose to continue the investigation, and shall endeavour to determine this constant in other ways.

THE METHODS OF SUGAR ANALYSIS.*

Determination of Water.

In Sugar or Massecuite.—Dry from 2 to 5 grms. in a flat dish (nickel or platinum) at the temperature of boiling water for ten hours; cool in a desiccator and weigh; return to the oven and dry for an hour. If on weighing there is only a slight change of weight, the process may be considered finished; otherwise the drying must be continued until the loss of water in one hour is not greater than 0·20 per cent.

In Honey or Molasses.—Proceed as above, using only 1 to 2 grms. of substance.

Density and Total Solids.

The density of juices, syrups, &c., is most conveniently determined by means of Baumé's or Brix's hydrometer or areometer, preferably with the latter, as the graduations of the scale give close approximations to the percentages of total solids. The Brix spindle should be graduated to tenths. It is therefore desirable for accuracy that the range of degrees recorded by each individual spindle be as limited as possible, this end being best secured by the employment of sets, consisting of not less than three spindles. The solutions should be as nearly as possible of the same temperature as the air at the time of reading, and if the variation from the standard temperature of the

* Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (American) at its Meeting at Chicago, August, 1893.

By the term "sugar analysis" it is understood that the analyses of all the common saccharine substances, viz., juices sugar, molasses, syrup, starch sugar, and honey, are embraced. In the following directions an attempt will be made to indicate the general principles which should guide the practice of sugar analysis, together with sufficient detail to enable these analyses to be carried out with accuracy and uniformity.

The principal components to be determined in the substances mentioned above are—

1. Water.
2. Density and total solids.
3. Ash.
4. Nitrogenous bodies.
5. Reducing sugar.
6. Sucrose.
7. Lactose.
8. Starch sugar.
9. Raffinose.

graduation of the spindle amounts to more than 1°, compensation therefore must be made by reference to tables of corrections for temperature.

Care should be observed in taking the density of a juice to allow it to stand in the cylinder until all air bubbles have escaped before reading the spindles. When it is desired to accurately determine the specific gravity of the sample, a specific gravity bottle or picnometer is employed.

The per cent of total solids can be approximately ascertained directly from the reading of the Brix hydrometer, or, knowing the reading of the Baumé spindle or the specific gravity of the sample, by reference to the table on page 214, *Bulletin* 31.

Determination of Ash.

(*a*) Heat 5 or 10 grms. of the material (sugar, molasses, honey) in a platinum dish* of 50 to 100 c.c. capacity at 100° until the water is expelled, and then slowly over a flame until intumescence ceases. The dish is then placed in a muffle and heated at low redness until a white ash is obtained.

For soluble ash digest the ash with water, filter through a Gooch crucible, wash with hot water, dry the residue at 100°, and weigh. The difference of weights equals soluble ash.

(*b*) Use 50 m.grms. of zinc oxide to 25 grms. of molasses or 50 grms. of sugar. Incorporate thoroughly by adding dilute alcohol and mixing; dry and ignite as above. Deduct the weight of zinc used from the weight of ash.

(*c*) Carbonise the mass at a low heat, dissolve the soluble salts with hot water, burn the residual mass as above, add the solution of soluble salts, and evaporate to dryness at 100°; ignite gently, cool in a desiccator, and weigh.

(*d*) Saturate the sample with H_2SO_4, dry, ignite gently, then burn in a muffle at low redness. Deduct one-tenth of the weight of the ash, then calculate the per cent.

(*e*) Dissolve 10 grms. of sugar in hot water and filter to remove sand, &c.; evaporate the filtrate and washings to dryness; carefully carbonise and extract with hot water until there is no longer any reaction for chlorine. Dry and ignite the residue; weigh as insoluble ash. Add the soluble portion, treat with HCl in slight excess, and evaporate to dryness. Heat until all free HCl is driven off; take up with water and a little HCl, filter, and wash. The residue is silica. Add NH_4OH to the filtrate, boil, and filter; wash the residue, which is iron oxide and alumina. To the filtrate add $(NH_4)_2C_2O_4$, evaporate to dryness, ignite and moisten with $(NH_4)_2CO_3$ and re-ignite, dissolve in water, filter, and wash. The residue on the filter represents calcium and magnesium carbonate. Evaporate the filtrate to a small bulk, add $(NH_4)_2CO_3$, and evaporate to dryness; drive off the excess of ammonia cautiously and weigh. This gives the alkalis as carbonates, and this weight, added to the insoluble ash, formerly determined, gives the total carbonate ash.

(*f*) Thoroughly mix 5 grms. of the material with a somewhat larger weight of pure quartz sand in a platinum dish; ignite in a muffle at a moderate red heat.

Alternate Method for Ash.

To avoid the correction of one-tenth, as proposed by Scheibler, and one-fifth, as proposed by Girard and Violette, when sugars are burned with H_2SO_4, Boyer suggests incineration with benzoic acid as giving the real quantity of mineral matter without correction.

The benzoic acid is dissolved in alcohol of 90 per cent, 25 grms. of the acid to 100 c.c. of alcohol; 5 grms. of the sugar are weighed in a capsule and moistened with 1 c.c. of water. The capsule is heated slowly in order to caramelise the sugar without carbonising it; 2 c.c. of the benzoic acid solution are next added, and the capsule warmed until all the alcohol is evaporated; the temperature is then raised until the sugar is converted into carbon. The decomposing benzoic acid produces abundant vapours, which render the mass extremely porous, especially if a circular motion is imparted to the capsule. The slow heating is continued until all the benzoic acid is volatilised.

The carbon obtained is voluminous and of a brilliant black colour. The incineration is accomplished in a muffle at a low red heat. The capsule should be weighed quickly when taken from the desiccator in order to avoid the absorption of water by the alkaline carbonates. Ammonium benzoate may be employed instead of benzoic acid, and the analyst should previously assure himself that neither the acid nor the ammonia salt leaves a residue on incineration. In addition to giving the mineral matters directly, this method permits the determination of their composition also, a matter of no small importance.

Determination of Nitrogen.

Any of the methods adopted by the Association for the estimation of nitrogen may be used.

Reducing Sugars.

Reagents (Soxhlet's Modification of Fehling's Solution).

1. 34·639 grms. of $CuSO_4,5H_2O$, dissolved and diluted to 500 c.c. with water. 2. 173 grms. of Rochelle salt, 50 grms. of NaOH, dissolved and diluted to 500 c.c. with water. Mix equal volumes of these solutions immediately before use. This mixture is the "mixed copper reagent" to be used for all the methods given below, except Allihn's method for dextrose, for which a special reagent must be used.

(*a*) *Approximate Volumetric Method for Rapid Work.*—Place 10 c.c. of the mixed copper reagent in a large test-tube and add 10 c.c. of distilled water. Heat to boiling, and gradually add small portions of the solution of the material to be tested, boiling to complete the reaction after each addition until the copper has been completely precipitated. Two minutes boiling is required for complete precipitation when the full amount of sugar solution has been added in one portion. When the end reaction is nearly reached and the amount of sugar solution to be added can no longer be judged by the colour of the solution, a small portion of the liquid is removed by means of Knorr's modification of Wiley's filtering tube (any other rapid means of filtration may be used that removes but a small portion of the hot liquid), is transferred to a small porcelain crucible or test plate, acidified with dilute acetic acid, and tested for copper with a dilute solution of potassium ferrocyanide. The sugar solution should be of such a strength as will give a burette reading of 15—20 c.c., and the number of successive additions should be as small as possible.

Since the factor for calculation varies with the minute details of manipulation, every operator must determine a factor for himself, using a known solution of a pure sample of the sugar that he desires to determine and keeping the conditions the same as those used for the determinations. For the standardisation of a solution for the determination of invert sugar in sugar-house products, dissolve 2·5 grms. of pure sucrose in 100 c.c. of water, add 10 c.c. of hydrochloric acid (specific gravity 1·188), and invert according to the method given below for double polarisation. Neutralise the acid with sodium carbonate and dilute to 1 litre. The 2·5 grms. of sucrose become 2·6316 grms. of invert sugar. The weight of invert sugar equivalent to 10 c.c. of the copper reagent is calculated as follows:—

$$\frac{2{\cdot}6316 \times \text{by number of c.c. of the standard sugar solution used}}{1000} = X,$$

the weight of invert sugar required to completely precipitate the copper in 10 c.c. of the reagent under the

* If the substance contains tin or any other metal capable of uniting with platinum, a dish made of some other material must be used.

conditions used for the test titration. For the calculation of the result of the titration of an unknown solution—

Let X = the factor obtained as above;

V = the number of c.c. of unknown sugar solution required to precipitate the copper from 10 c.c. of copper solution;

W = the weight of the material under examination in 1 c.c. of the solution.

Then $\frac{100\,X}{V\,W}$ = per cent of invert sugar in the sample.

The calculation can be much simplified by so standardising the copper reagent that 50 m.grms. of invert sugar will be required to reduce the copper from 10 c.c. of the copper reagent. The various tables given in works on sugar analysis then become applicable. These tables are arranged for a "glucose normal solution" containing 5 grms. of the material to be examined in 100 c.c. When the weight per 100 c.c. is more or less than 5 grms., the number found in the table is increased or diminished accordingly.

(*b*) *Soxhlet's Exact Volumetric Method.*—A preliminary titration is made to determine the approximate percentage of reducing sugar in the material under examination. A solution is then prepared which contains approximately 1 per cent of reducing sugar. Place in a beaker 100 c.c. of the mixed copper reagent, and approximately the amount of the sugar solution for its complete reduction. Boil for two minutes. Filter through a plaited filter and test a portion of the filtrate for copper by use of acetic acid and potassium ferrocyanide. Repeat the test, varying the volume of sugar solution, until two successive amounts of sugar solution are found, which differ by 0·1 c.c., one giving complete reduction and the other leaving a small amount of copper in solution. The mean of these two readings is taken as the volume of the solution required for the complete precipitation of 100 c.c. of the copper reagent.

Under these conditions 100 c.c. of the mixed copper reagent require 0·475 grm. of anhydrous dextrose, or 0·494 grm. of invert sugar for complete reduction. The percentage is calculated by the following formula:—

W = the weight of the sample in 1 c.c. of the sugar solution;

V = the volume of the sugar solution required for the complete reduction of 100 c.c. of the copper reagent.

Then $\frac{100 \times 0{\cdot}475}{V\,W}$ = per cent of dextrose,

or $\frac{100 \times 0{\cdot}494}{V\,W}$ = per cent of invert sugar.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Anniversary Meeting, March 22nd, 1894.

Dr. Armstrong, President, in the Chair.

The President delivered an Address, giving expression to the views that he had been led to form during his long official connection with the Society, and claiming for it the right to exercise far wider functions in the future on the ground that, although named the Chemical Society of *London*, it may now be regarded as the embodiment of the interests of chemical science in the United Kingdom.

Before presenting the Longstaff Medal, he referred to Dr. Longstaff's death in the interval since the last award of the medal, and to the lively interest which the founder of the research fund took in our affairs up to the very last; also to Mr. Mond's donation of £100 to the fund during the year; and to the income of the fund and the importance of securing further contributions. In presenting the medal to Mr. Horace T. Brown, F.R.S., the President referred to his early career, and the importance of the services he had rendered to chemical science, not only directly but also indirectly, by introducing scientific practices into the brewing industry.

The following statistics were referred to:—

Number of Fellows, March, 1893		1895
Since elected who have paid their fees		140
		2035
Removed on account of non-payment of fees	33	
Withdrawn	22	
Deceased	19	
	—	74
Present number of Fellows		1961
Number of Foreign Members		33

The following Fellows have died within the year:—J. T. Brown, J. H. Bicket, Dr. James Blake, Russell Carew, Col. F. C. H. Clarke, R. H. Davies, William Foster, Samuel Gale, C. H. Heaton, H. R. Hind, Hodgson Jones, Dr. A. Leibius, S. A. Phillips, H. D. Pochin, Charles K. Scott, W. B. Tustin, H. B. Thornton, John Tyndall, F.R.S., and John Woodland.

The following Fellows have withdrawn from the Society:—Harold Alger, Dr. E. J. Ball, J. B. Barlow, Thomas Beesley, F. W. Boam, George Collar, Dr. T. Cooksey, J. H. Dagger, Rev. G. Daubeney, Clement Higgins, Walter Hogben, U. A. Jackson, J. F. McArthur, J. C. Mulrean, G. Gordon Parker, Henry Piele, H. Pilkington, T. W. Shore, A. J. Smith, Rev. C. J. Taylor, A. Trobridge, and A. Wingham.

The names of the following Fellows have been removed from the register, having ceased to be Fellows owing to non-payment of the subscription:—Dr. L. Bernstein, T. F. Barbour, P. C. Bunn, R. G. Christopher, Adolph Dresel, A. C. Diogo, R. S. Edwards, G. W. Gibson, T. A. Hedley, Rev. H. Heap, A. C. Holborn, A. H. Jackson, J. C. Jackson, A. H. Knight, F. T. Knott, T. H. Leeming, Dr. C. Morfit, J. L. MacMillan, Dr. W. Mackey, W. E. Matthews, Frank Mousley, W. B. Nesbit, W. S. Newman, T. A. Pooley, G. L. Rait, A. P. Smith, J. Snodgrass, R. St. Stephens, P. Y. Sheshadri, F. W. Shaw, James Sibun, H. K. Tompkins, and E. W. Whieldon.

The Society has lost one of its foreign members, Edmond Frémy, who died early in March.

Although the increase in the number of Fellows during the year is satisfactory, and the number large, when it is considered how wide are the applications of chemical science, and that the aid of the chemist must ere long be recognised as essential to the prosperity of a majority of industries, the Society should be able to count on a far larger measure of support in the future—certainly every member of the Society of Chemical Industry should belong to it, and many pharmacists. Discussing the question of qualification for the Fellowship, the President expressed the opinion that it would probably be advantageous to remove the word "qualification" from the certificate, and to adopt a principle of absolute free trade, such as prevails in the sister society in Berlin, with the object of interesting as many as possible in the work of the Society.

The misuse of the letters F.C.S. was adverted to.

The Society's publications were next considered. The 1893 volume of *Transactions* contains no fewer than 104 papers, occupying 1432 pages, that published in the previous year having contained only 90 papers, occupying 1096 pages. Of the two volumes of Abstracts published in 1893, the organic section contains 1228 notices, occupying 744 pages; whilst the general section contains 1418 abstracts, occupying 612 pages. The index

to the *Transactions*, *Abstracts*, and *Proceedings* occupies no fewer than 158 pages. Compared with those of the previous year, these statistics indicate that 296 more papers have been abstracted, although from the more concise style of abstracting adopted, the abstracts are contained in 180 fewer pages. The number of communications made to the Society during the session has been 131.

After pointing out that chemical literature is fast becoming unmanageable and uncontrollable from its very vastness, the President proceeded to argue that it would be of great advantage to centralise the publication of chemical papers as far as possible, and that there should be one journal for each country. No fewer than 2500 copies of the Society's journal went into circulation, and the Society had now so thoroughly established its position, and was so far reaching in its organisation, that it had a right to expect—indeed demand—the support of British chemists generally. It must be to the advantage not only of English speaking chemists, but of chemists throughout the world, that such support should be accorded to it.

Having discussed this subject at length, and the relation of the Society to other bodies, including the Royal Societies of London and Edinburgh, the attitude of authors communicating their papers elsewhere was commented on, and the necessity of consolidating the interests of chemists in this country in order that their work may be treated with the respect it deserves was emphasised.

The importance of action being taken by the Society of Chemical Industry to focus all information relating to applications of chemical science to industry was then referred to; and also the desirability of steps being taken to organise a system of publishing physical papers and abstracts, the hope being expressed that the Physical Society of London would soon undertake this work.

The necessity of greater care being taken by authors in the preparation of their papers next came under discussion, greater conciseness being advocated, as well as more attention to literary style.

The abstracts of papers published elsewhere were referred to as very satisfactory on the whole, although they could not be regarded as by any means a complete presentment of the work that was being done. The necessity of occasionally monographing the state of knowledge with regard to various special fields of work was referred to, and the hope expressed that before long arrangements would be made to place such accounts in the hands of the Fellows.

The character of the *Proceedings* was then considered, and the opinion expressed that this should be in every way an official publication, entirely under the control of its recognised official editors.

The additions to the library having been noted, reference was made to the near approach of the time when the shelf room would be exhausted. The probable insufficiency at no distant date of the accommodation afforded by the meeting room was also commented on. The expectations that the structural alterations made during the previous year and the introduction of the electric light would greatly conduce to the comfort of those attending the meetings have been fully confirmed during the session. The objects to be secured by the meetings were next considered.

The publication of the Stas and Kopp memorial lectures was noted. The delivery of addresses in memory of von Hofmann having been commented on, reference was made to Dr. Caro's monograph giving the history of the development of the coal-tar colour industry, in which von Hofmann's influence was very fully taken into account, and to the lessons to be learnt from the contemplation of von Hofmann's career.

Referring next to the events of the year which are of interest to chemists, mention is first made of the Rothamsted jubilee, and to the public recognition of Dr. Gilbert's great services which it had involved.

The equipment of a laboratory for its examinations by the Institute of Chemistry is spoken of as a step which cannot fail to have most important results, and which may be said to have established the Institute on a firm basis. The inestimable value of a broad training such as is now demanded of candidates by the scheme introduced by the late President, Prof. Tilden, is also referred to.

Other topics dwelt on are the establishment of a research department in connection with the Imperial Institute charged with the examination and exploitation of the innumerable natural products from India and the Colonies collected together at the Institute; the establishment in London of the Institute of Preventive Medicine; and the appointment of inspectors by the Science and Art Department, whose duty it will be to take cognisance of the manner in which teaching is being carried on and to advise the teachers.

The action taken by the Royal Society of London in issuing a circular to the scientific world suggesting that from the beginning of the coming century complete authors and subject catalogues of science should be prepared by *international co-operation* is next brought under notice, and the importance of making any future index of chemical work a classified index is dwelt on. Lastly, reference is made to the report relating to the establishment of a teaching university in London and to the appointment of the Commission on Secondary Education.

He had always thought, said the President, that it should be the duty of the occupant of the chair to deliver an address on a chemical subject, and he had been surprised to find how uniformly previous Presidents had refrained from so doing: he now realised, however, how difficult it was to avoid political subjects and how easy therefore to avoid scientific subjects. There are, however, a multitude of scientific questions, the discussion of which at the present time would be of great interest, such as—to mention but a few—the relation of physical properties to structure, and the properties of elements such as nitrogen, and, indeed, elements generally, as dependent on the structure of the molecules in which they are contained; or the fundamental principles on which structural formula generally are based, including the discussion of von Baeyer's very remarkable experimental investigations of benzene derivatives; or the laws of substitution; or valency; or alloisomerism; or bacteriology and its general bearings on the question as to the nature of the chemical changes attendant on life; including the discussion of the supposed assimilation of nitrogen by plants; or, lastly, the general bearings of the highly specialised observations which constitute the work of the day; on each of which subjects a lengthy essay might be written if only time and space were at disposal. The interdependence of chemical and electrolytic change being a subject which has given rise to much discussion, and being of such fundamental importance at the present time, he is led to devote some space at the close of the address to a consideration of this subject more in detail.

Sir Frederick Abel proposed a vote of thanks to the President coupled with the request that he would allow his address to be printed. This was seconded by Dr. Russell, and carried unanimously.

The Treasurer then gave an account of the Society's income and expenditure during the past session. The receipts by admission fees and subscriptions had been £3887 6s. 8d., as against £3771 11s. 4d. in the previous year; £424 11s. 6d. had been realised by the sale of the Journal, practically the same amount as in the previous year. The year's dividends amounted to £367 2s. 7d., and the balance at the bank was £1842 1s. 10d., as against £1511 17s. 1d. in the previous year. The Journal had cost £2882 17s. 3d., instead of £2745 7s. 4d.; the expenditure on the library amounted to £497 0s. 9d.; the *Proceedings* cost £215 16s. 5d.; the total expenditure being £4395 8s. 3d. Grants amounting to £185 had been made from the Research Fund.

Mr. WARINGTON proposed, and Mr. PICKERING seconded, a vote of thanks to the Treasurer, which was carried. Professor THORPE, after replying, proposed a vote of thanks to the Auditors; this was seconded by Mr. PAGE and carried.

A vote of thanks to the office bearers and Council was proposed by Dr. STEVENSON, seconded by Dr. MESSEL, and carried. Professor THOMSON replied.

Mr. HORACE T. BROWN proposed, and Dr. J. A. VOELCKER seconded, a vote of thanks to the Editors, Abstractors, and Librarian. Mr. GROVES replied.

A ballot was then taken, when the following were declared by the scrutators elected as Officers and Council for the ensuing session:—

President—H. E. Armstrong, LL.D., Ph.D., F.R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; A. Crum Brown, M.D., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; Sir J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Lord Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

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ROYAL INSTITUTION OF GREAT BRITAIN.

Annual Meeting, Tuesday, May 1, 1894.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

THE Annual Report of the Committe of Visitors for the year 1893, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Real and Funded Property now amounts to above £102,000 entirely derived from the contributions and donations of the Members and of others appreciating the value of the work of the Institution.

Sixty-two new Members were elected in 1893.

Sixty-three Lectures and nineteen Evening Discourses were delivered in 1893.

The Books and Pamphlets presented in 1893 amounted to about 250 volumes, making, with 584 volumes (including periodicals bound) purchased by the managers, a total of 834 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland, K.G., D.C.L., LL.D.

Treasurer—Sir James Crichton-Browne, M.D., LL.D., F.R.S.

Secretary—Sir Frederick Bramwell, Bart., D.C.L., LL.D., F.R.S., M.Inst.C.E.

Managers—Sir Frederick Abel, Bart., K.C.B., D.C.L., LL.D., F.R.S.; Captain W. de W. Abney, C.B., D.C.L., F.R.S.; The Right Hon. Lord Belhaven and Stenton; John Birkett, F.R.C.S.; Edward Frankland, D.C.L., LL.D., F.R.S.; Sir Douglas Galton, K.C.B., D.C.L., LL.D., F.R.S.; Robert Hannah; William Huggins, D.C.L., LL.D., F.R.S.; Alfred Bray Kempe, M.A., F.R.S.; George Matthey, F.R.S.; Ludwig Mond, F.R.S.; Hugo Müller, Ph.D., F.R.S.: Sir Andrew Noble, K.C.B., F.R.S., M.Inst.C.E.; William S. Playfair, M.D., LL.D., F.R.C.P.; Basil Woodd Smith, F.R.A.S., F.S.A.

Visitors—Charles Edward Beevor, M.D., F.R.C.P.; Francis Woodhouse Braine, F.R.C.S.; Arthur Carpmael; Joseph Gordon Gordon, F.C.S.; Carl Haag; Donald William Charles Hood, M.D., F.R.C.P.; John Imray, M.A., M.Inst.C.E.; Raphael Meldola, F.R.S.; Hugh Leonard; Lachlan Mackintosh Rate, M.A.; Boverton Redwood, F.C.S.; Sir Owen Roberts, M.A., D.C.L., F.S.A.; John Bell Sedgwick, J.P., F.R.G.S.; Judge Frederick Meadows White, Q.C.; Wm. Henry White, C.B., LL.D., F.R.S.

NOTICES OF BOOKS.

Odorographia: A Natural History of Raw Materials and Drugs Used in the Perfume Industry, including the Aromatics Used in Flavouring. Intended for the Use of Growers, Manufacturers, and Consumers. By J. CH. SAWER, F.L.S. Second Series. London: Gurney and Jackson (successors to Mr. Van Voorst). Brighton: W. J. Smith. 1894. 8vo, pp. 523.

SOME time ago we had the pleasure of examining and noticing the first series of this valuable and interesting work, and we now welcome the second volume. Hitherto perfumes have in English scientific and technical literature enjoyed a share of attention remarkably small either from a chemical or a biological point of view, or as regards the extensive trade of which they form the subject. The misfortune is that as yet we are unable to define perfumes as distinct from evil odours. It is probable that some of the substances included in the present work would be relegated by many persons to the latter class. We need merely mention buchu, chamomile, fennel, and tansy. We may remark that the function of the pleasant odours given off by so many plants has been determined. But why the stench-worts—if we may be permitted so to call them—have been endowed with their offensive smells is still an unsolved problem. Their disagreeable emanations do not appear to keep off any enemies.

Turning to a very different subject we notice that the sophistication of essential oils is carried on with great diligence and skill, whilst the tests for recognising its purity are not to be depended upon under all circumstances. English oil of peppermint is so largely mixed with the American and Japanese products that it can be no longer recognised. It is to be feared that the manufacturers and merchants often work under the advice of able chemists. These gentlemen may, in apology, plead the example of eminent counsel whose conscience permits them to hold briefs for men whom they know to be quacks of the most dangerous grade.

Mr. Sawer, in his list of errata, refers to, and in a way half apologises for having in his first series spoken of "coker" nuts. He tells us that this kakography is used by the large fruit importers of London. Unfortunately, many people in London take unwarrantable liberties with the letter *r*, omitting it where it ought to be used, and inserting it where it has no right to be present. Unfortunately, also, three important vegetable products have their names habitually confounded in "English as she is spoke": the cocoa-nut, the fruit of *Cocos nucifera*, the chocolate-nut or bean, the product of the orchid *Theobroma cacao*, and the coca or cuca of South America, yielded by *Erythroxylon coca*. Perhaps to get rid of this confusion it might be well to call the first-mentioned fruit *cocos*-nut, retaining its botanical name.

Mr. Sawer's valuable, elaborate, and trustworthy compilation will be of immense value to the interests whom it more especially concerns. We hope that it may have the effect of encouraging planters to take up more systematically the production of the perfume plants, and technical chemists to develope this promising industry.

CORRESPONDENCE.

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

To the Editor of the Chemical News.

SIR,—The Executive Committee of the Association of Official Agricultural Chemists has decided to call the Annual Meeting of the Association for August 23, 24, and 25, 1894. The meetings will be held in the Lecture Room of the National Museum at Washington, beginning at 10 o'clock on Thursday, August 23.

The reporters for the meeting are as follows:—

Phosphoric Acid—B. W. Kilgore, Raleigh, N.C.
Nitrogen—J. M. Bartlett, Orono, Mo.
Potash—H. J. Wheeler, Kingston, R.I.
Soils and Ash—A. M. Peter, Lexington, Ky.
Dairy Products—F. H. Farrington, Champaign, Ill.
Foods and Feeding Stuffs—H. J. Patterson, College Park, Md.
Fermented Liquors—Geo. F. Colby, Berkeley, Cal.
Sugar—G. L. Spencer, Washington, D.C.

The co-operation of European chemists has been invited in the analytical work, and several acceptances of the invitation have been received. It is urged upon all members who have communications to make to the Association to bring them properly prepared and ready for printing. Much delay has arisen heretofore in securing the manuscript promptly from the reporters and others presenting papers. The speedy publication of the proceedings will be greatly facilitated by bringing everything properly prepared.—I am, &c.,

H. W. WILEY,
Chief of the Division of Chemistry
and Secretary of the A.O.A.C.

Washington, D.C., April 13, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 16, April 16, 1894.

We find that M. Grimaux has been elected a Member of the Chemical Section of the Academy, vice the late Professor Fremy.

Electrochemical Means of Observing Alternating Currents.—P. Janet.—The measurements of alternating currents present two peculiar elements, nothing analogous to which is found in the case of continuous currents: the frequencies and the differences of the phases. Hitherto no great importance has been attached to the measure of the frequencies; but there are cases where it is well to measure them directly, *e.g.*, that where a laboratory receives an alternating current from a remote central station. As regards the difference of phases, it is important to institute a simple method, fairly exact for ordinary cases. To this end the author arranges on metallic registering cylinder a sheet of paper steeped with the solution of potassium ferrocyanide and ammonium nitrate as used in Bain's electrochemical telegraph. On this paper there acts a style of iron or steel. He makes communication with the cylinder on the one hand, and the point of iron on the other, with the two points between which he wishes to study the periodic electromotive force. If the cylinder is caused to rotate rapidly he obtains a discontinuous trace of Prussian blue, the maxima of which correspond to the maxima of the electromotive force in question.

The Allotropic Transformation of Iron.—Georges Charpy.—The author has been previously led to conclude that the existence of a rectilinear tract in the traction curves of re-tempered iron and steel is characteristic of an allotropic transformation of the metal. The author explains his views by means of a diagram.

Journal fur Praktische Chemie.
New Series, Vol. xlix., Parts 5, 6, and 7, 1894.

New Contributions to the Question of the Constitution of Benzol.—J. W. Brühl.—The author gives at great length a general view of the physical and chemical results hitherto obtained, gives new observations, describes the physical constants of hexamethylene, and the volumetric, spectrometric, and thermochemical researches.

Researches from the Laboratory of the University of Freiburg, in Breisgau.—These researches comprise a paper on the alkylate derivatives of isochinoline, by Ad. Claus; a memoir on the benzol-nucleus, by W. Vaubel; and a memoir on the constitution of the triphenyl-methane tinctorial substances, by A. Rosenstiehl. This last paper criticises certain unfounded claims of priority advanced by Stock.

Some New Syntheses of Diketochinazoline.—A. Stewart.—A preliminary communication.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 98.

Influence of Saline Matters contained in Waters Used in Malting and Brewing.—E. Fleurent.—This paper is to a great extent a reproduction of two memoirs submitted by Mr. Matthews to the Institute of Brewing, London, and published in its *Transactions* for March and May, 1893.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., No. 4.

Presence of Camphene in Essential Oil of Spike.—G. Bouchardat.—Oil of spike, though almost entirely composed of camphor, linalol, and a little borneol and their isomers, contains small quantities of a hydrocarbon, $C_{20}H_{16}$, boiling at 158°.

Volatile Carbides of Essence of Valerian.—M. Oliviero.—Essence of valerian contains in its most volatile parts a notable portion of carbides, $C_{20}H_{16}$, which have hitherto been assimilated to a turpentine. On examining these fractions the author finds that they are mere camphene associated with turpentine.

An Apparatus for Generating Weak Currents of Carbon Dioxide.—Greiner and Friedrichs (*Zeitsch. fur Angew. Chemie*).—Into a bottle provided with a tightly-fitting caoutchouc stopper and a gas-delivery tube there is introduced a permeable earthen cyanide which takes up the acid, whilst the bottle is then filled up with a solution of sodium hydrocarbonate. The acid soaks slowly through the pores of the cylinder, and thus generates a slow current of gas.

MEETINGS FOR THE WEEK.

Monday, 7th.—Society of Arts, 8. (Cantor Lectures). "Typewriting Machines," by Henry Charles Jenkins, A.M.Inst.C.E.
—— Royal Institution, 5. General Monthly Meeting.
—— Medical, 8.30.
—— Society of Chemical Industry, 8. "The Commercial Electrolysis of Fused Salts," by Claude Vautin. "Testing of Hydraulic Cements," by W. H. Stanger, M.Inst.C.E., and Bertram Blount, F.I.C., F.C.S.

Tuesday, 8th.—Royal Institution, 3. "Rubies—their Nature, Origin, and Metamorphoses," by Prof. J. W. Judd, F.R.S.
—— Society of Arts, 8. "Pewter," by J. Starkie Gardner.
—— Medical and Chirurgical, 8.30.
—— Institute of Civil Engineers, 8.
—— Photographic, 8.

Wednesday, 9th.—Society of Arts, 8. "Telegraphs and Trade Routes in Persia," by Colonel Wells.
—— Geological, 8.

Thursday, 10th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "The Solid and Liquid States of Matter," by Prof. Dewar, F.R.S.

Friday, 11th.—Royal Institution, 9. "English Folk Song," by the Rev. S. Baring-Gould, M.A.
—— Astronomical, 8.
—— Physical, 5. "On Electromagnetic Induction in Plane Cylindrical and Spherical Current Sheets," by G. H. Bryan, M.A. "On Dielectrics," by R. Appleyard.

Saturday, 12th.—Royal Institution, 3. (The Tyndall Lectures). "On Colour Vision," by Capt. Abney, F.R.S.

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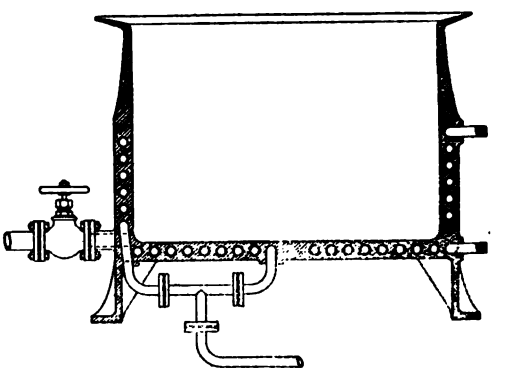

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says:—

P. 316. "An improved vessel for boiling oil, and suitable for many other kindred purposes, has been recently described by T. Frederking (Chemical News, London). A coil of stout piping is arranged in a casting mould, so that the molten metal forming the pan is cast round the coil, much as is done in the case of the water-tuyeres of a blast furnace. Steam at any pressure [or any other heating medium] being passed through the coil, the pan is heated up proportionately without any danger, the pressure bearing solely on the piping and not on the metal pan itself, whilst the well conducting metal walls allow the heat to pass readily. Temperatures up to 350° and 400° C. can be thus obtained."

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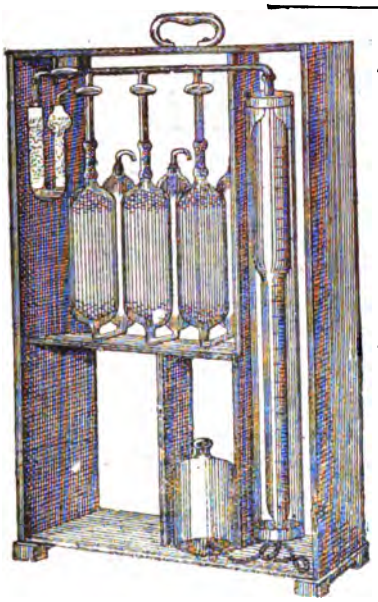

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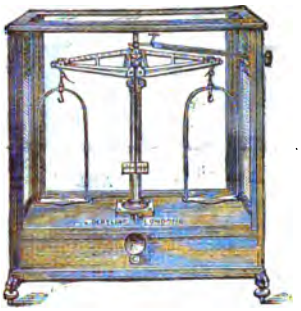

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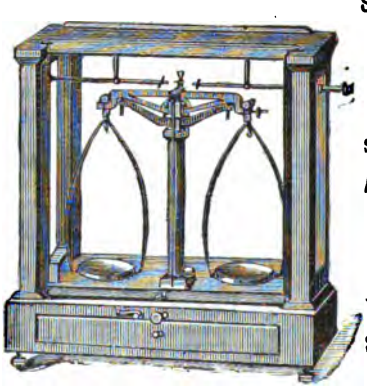

FIG. 3a.

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VOL. LXIX., No. 1798.

A COMBINATION LABORATORY LAMP, RETORT, AND FILTER STAND.*

By A. LIVERSIDGE, M.A., F.R.S.,
rofessor of Chemistry in the University of Sydney.

THE stand, as will be seen from the figure, is fitted with:—

A brass screw clamp (*a*).

Two or more adjustable brass retort or filter rings, which can be placed on the rod by the lateral slit at (*b*).

An Argand burner (*c*), on its peg (*a*), with regulator and copper chimney or shade; this is perforated so as to allow of its being used as a support for dishes, watch glasses, or crucibles. With a glass chimney the Argand can be used for illumination purposes.

A support or peg for the Argand or Bunsen burner when not in use (*d*).

Retort and filter ring rod (*e*); this is attached to the foot (*j*) of the lamp by a bayonet joint not shown in the woodcut.

An ordinary fish tail jet (*f*), on its peg, for glass bending or illumination.

A blowpipe jet (*g*) on its peg.

A Bunsen burner (*h*), provided with an air regulator at (*i*), and a gallery for the support of the draught shade or chimney (*l*).

The foot (*j*) is made of lead instead of iron for the sake of increased stability and to prevent rusting; it also is made to rest on three points for greater steadiness and to keep it out of liquids which may happen to be spilt on the bench.

A more convenient position for the supply tap (*k*) is at the side at (*j*).

There is also a rose burner, not shown in figure, to drop over the Bunsen burner.

All the parts are interchangeable and are provided with ground joints so as to avoid the inconvenience of their becoming fixed, as often happens with screw joints.

When the Argand or other jet is required for use, the Bunsen burner is placed on the peg at the back, from which the former burner or jet has been removed, so that there is no need for any of the parts to get astray when not in use.

* Exhibited before the Royal Society of New South Wales, September 6, 1893.

ON THE QUANTITATIVE ELECTROLYTIC DETERMINATION OF LEAD.

By A. KREICHGAUER.

IN a previous communication, Prof. Medicus has proposed two methods for the quantitative determination of lead in galena (*Berichte*, xxv., 2490). In both the lead is to be ultimately weighed as peroxide. The first method precipitates electrolytically, the other throws it down from an alkaline solution by means of bromine. I have worked out these proposals closely, and shall shortly report elsewhere at length on the results obtained. Here I wish merely to give for the present a preliminary report on a portion of the subject, and especially on the influence of the concentration of the nitric acid upon the electrolytic precipitation.

From a number of experiments it appears that the use of a nitric mixture of 1 part acid (sp. gr. 1·4) and 7 parts water, followed by two washings with alcohol, is the most satisfactory.

The by-experiments gave also the following results:—

1. Concerning the manner of drying.

Lead peroxide not washed with alcohol is ready for weighing after drying for fifteen minutes; it being indifferent whether the temperature employed is 110° or 200°.

Peroxide washed with alcohol is ready for weighing after being heated at 120° for five minutes. A prolonged exposure to higher temperatures has no influence. Hence it appears that not the manner of drying, but the relative proportions of acid and water and the treatment of the peroxide with alcohol modify the results.

The experiments were continued for a longer time as an excessive duration of the analysis occasions the lead to be re-dissolved (*Bericht des Münchener Laboratoriums*).

Some of the analyses were exposed for forty-eight hours to a current equal to 0·2 c.c. detonating gas per minute. No lead could be detected in the solution.

The magnitude of hygroscopicity was observed.

The treatment of the electrolytically deposited peroxide with absolute alcohol reduced the hygroscopic character of the deposit, and consequently the error in the electrolysis is reduced on washing twice with alcohol.

The increase of weight of the peroxide according to the relative moisture of the air is completed in some operations in from six to fifteen minutes. The maximum weight in default of washing with alcohol was reached in forty-five minutes, even when the platinum capsule is allowed to stand in the balance case (in which calcium chloride was kept). If, after reaching the maximum weight, the capsule is removed from the balance case and allowed to stand in the open for from twelve to twenty hours the weight generally remained constant, but sometimes it increases a few tenths of a m.grm.

The most striking fact is that the attraction for water does not depend on the quantity of lead peroxide deposited.

The cause is a minimum proportion of nitric acid. This acid is not easily and completely removed by washing with water. The precipitate, even if heated with water to 50°, did not give the nitric acid reaction with brucine, whilst the reaction became distinct after heating with potassium carbonate. The proportion of nitric acid in the precipitate is therefore the cause that analyses executed under apparently identical conditions gave unequal results. The smaller the quantity of the peroxide, the greater may be the error in the analysis. In a precipitate of 0·15 grm. lead peroxide, the percentage in-

crease amounts to +0·42 per cent, and the maximum error 0·42 − 0·8 = 0·34 per cent of lead; whilst in a precipitate of 0·5372 grm. the difference was −0·02 + 0·1.

In conclusion, I must give an explanation how the results were obtained.

The capsule, when cool, was laid upon the scale, the weights were laid in counterpoise, and the first even position was noted.

In the last experiments made, in contradistinction to former experience, large quantities of lead were submitted to electrolysis. Classen states in his "Quantitative Electrolysis" that more than 0·2 grm. lead peroxide can be accurately weighed; whilst von Miller and Kiliani even cause 1 grm. lead nitrate to be electrolysed. The latter, indeed, with the precaution that any detached particles of lead peroxide are collected on a filter and weighed separately. The greatest cleanliness (as in all electrolytic operations) being pre-supposed (heating the platinum capsule before the analysis in concentrated potassa-lye and then in concentrated nitric acid) as much as 1·8 grms. (1877) lead peroxide may be firmly deposited on a surface of 139 square c.m. The regular use of a capsule for the separation of lead as peroxide seems to be very advantageous. The position of the electrode with reference to the capsule is of the greatest importance in the analysis of large quantities of lead. In this case the electrode is immersed at about half the depth of the capsule—better higher than lower—by which means, after the completion of the deposit, the lead peroxide can be conveniently washed by means of a syphon without loss and without interruption of the current. The current must, of course, be intensified in these analyses. (Source of current, four Meidinger elements). At the outset 0·2 c.c. detonating gas per minute are sufficient, and afterwards 0·4 c.c.

The analyses were generally allowed to proceed during the night, the duration being fourteen hours.

Classen's well-known capsule was used with a disc electrode. The dimensions are as follows:—Height, 4·5 c.m.; diameter, 10·1; weight, about 50·0 grms. At a distance of 9 m.m. from the precipitate to the edge of the capsule the coated surface was 138·6 square c.m.

I shall subsequently report on the application of electrolytic precipitation in the analysis of galena, and on the influence of antimony.—*Berichte der Deut. Chem. Gesell.*, xxvii., p. 315.

THE DETECTION OF AMMONIA BY NESSLER'S SOLUTION.

By L. L. DE KONINCK, D.Sc.

About a year ago, having had occasion to confirm the presence of traces of ammonia in the distillate from an alcoholic mixture, in which I had serious reasons to suspect its presence, I naturally had recourse to Nessler's solution. This test not giving me the expected reaction I tried that recommended by Bohlig,* viz., mercuric chloride, and obtained a decided reaction.

I repeated these tests, and somewhat modified the conditions of the experiment, and found that alcohol had always a marked influence on the sensitiveness of the reaction.

Not attaching much importance to this observation I did not make any quantitative estimations, but contented myself with communicating what I had observed to my illustrious colleague Prof. Fresenius, in a letter which I sent him on December 12th, 1892. From this letter he published an extract in his translation of the second part of the *Zeitschrift für Analytische Chemie*, xxxii., p. 188, 1893.

Some time after B. Neumann contested the accuracy of my observations (*Chemiker Zeitung*. xvii., p. 880, June 21, 1893). According to him I was absolutely mistaken in such a simple experiment, and, contrary to my statements, Nessler's solution should give, with *traces* of ammonia, a perfectly distinct reaction (*ganz deutliche Reaktion*) as well in water containing from 1 up to 50 per cent of alcohol as in pure water; it also should give a distinct reaction (*deutliche Reaktion*) in absolute alcohol.

The author has thus obtained, I may observe, an appreciable difference when using an alcoholic solution. He attributes the result of my experiment to the use of a badly prepared reagent or one that may have changed owing to having been kept too long. But that will not explain the differences I obtained when treating side by side, in the same manner, aqueous and alcoholic solutions.

It is true that in the short note appearing in the *Zeit. f. Anal. Chemie* no mention of these experiments was made. Further, there was an excusable confusion in the meaning attributed to the word "*acoolique*," translated as "*alkoholisch*," which I used for describing the solutions which I employed; I meant to express by that word ammoniacal solutions *in alcohol*, while my esteemed opponent took it to mean *containing alcohol*.

It nevertheless remains that he obtained a distinct reaction with traces of ammonia in a solution of absolute alcohol, while I not only found no precipitate of mercuric oxyamido iodide, but did not even succeed in obtaining a similar colouration.

It was therefore most important that I should repeat my experiments to decide whether or no I was mistaken. This time I determined to work, so to speak, quantitatively, and not to be contented with vague or incomplete indications insufficient to make it possible to repeat any experiment under identical conditions.

What must be understood by *traces* of ammonia? What difference is there between a *distinct reaction* and a *perfectly distinct reaction?* What proportion of reagent did M. Neumann employ. Nothing was precise.

My colleague having suggested that the reagent I used might be called in question,* I took particular care in this instance to prepare it myself and to use it immediately.

Fresenius gives two different formulæ for the preparation of Nessler's solution; one† recommending the direct use of mercuric iodide; in the other, that indicated by M. Neumann,‡ the chloride is employed. In the former there are 2 grms. of potassic iodide to each 50 or 55 c.c. of reagent, or 35 to 40 grms. per litre; in the latter there are similarly 35 grms. per litre, but half of it is used to transform the mercuric chloride into iodide; there thus remains but 17·5 grms.

In face of this difference I thought it necessary to experiment with both solutions.

Kubel-Tiemann gives still another formula analogous to the second, described above; but I did not consider it necessary to make use of it.

My experiments were carried on side by side with a 2 per cent aqueous solution of mercuric chloride.

I started with an alcoholic solution of ammonia, titrating 0·0086 grm. NH_3 per c.c.; 10 c.c. of this solution were diluted to 500 c.c., one part with water, the other with absolute alcohol. These two solutions, therefore, each contained 0·172 m.grm. of ammonia per c.c., being thus almost centinormal. The subjoined Table gives the results of my experiments.

It will be seen that these results confirm absolutely what I previously stated. They show that, for *traces* of ammonia, that is to say in the only case when one has

* This reaction has been long known; it was pointed out in "A Practical Treatise on the Use and Applications of Chemical Tests," 2nd Edition, 1818, by F. Accum, who attributed it to F. Brande.

* Having previously used the solution which was in general use in the laboratory I cannot absolutely guarantee its purity.

‡ "Analyse Qualitative," 5th Edition, p. 104. In this formula the author employs a *concentrated solution* of potash; in the absence of more precise information I made use of a solution obtained by dissolving one part by weight of commercial potash in two parts of water.

† "Analyse Quantitative," 6th Edition, p. 718. The formula gives the choice of either potassic or sodic hydrate; I made use of the potassic.

No.	Alcoholic Ammonia.	Aqueous Ammonia.	Ammonia in m.grms.	Alcohol.	Water.	Per cent of Ammonia in the mixture.	Volume in c.c. and nature of reagent employed. (*a*)	Results. Immediate.	Results. After 24 hours.
	C.c.	C.c.		C.c.	C.c.				
1	1	—	0·172	5	—	0·029	$\frac{1}{2}N_1$	Yellowish cloudiness.	Yellowish deposit.
2	1	—	,,	5	—	,,	$\frac{1}{2}N_2$	White cloudiness.	Slight yellowish deposit.
3	—	1	,,	—	5	,,	$\frac{1}{2}N_1$	Normal brown cloudiness, translucent.	Dark brown deposit.
4	—	1	,,	—	5	,,	$\frac{1}{2}N_2$	Faint cloudiness, brown transparent liquid.	Slight light brown deposit.
5	1	—	,,	5	—	,,	1Hg	Slight white cloudiness.	Slight white deposit, flocculent.
6	—	1	,,	—	5	,,	1Hg	Intense cloudiness, rather slower.	Slight white deposit, flocculent.
7	5	—	0·860	10	—	0·057	$1N_1$	Intense yellowish precipitate.	Strong brownish deposit, covered with a white layer.
8	5	—	,,	10	—	,,	$1N_2$	Whitish cloudiness, not very strong.	Yellowish brown deposit, covered with a white layer.
9	5	—	,,	10	—	,,	1Hg	White cloudiness, less strong than No. 7.	White deposit.
10	—	5	,,	—	10	,,	$1N_1$	Normal reaction very intense, opaque liquid.	Strong light brown deposit.
11	—	5	,,	—	10	,,	$1N_2$	The same less intense, liquid slightly translucent.	Strong light brown deposit.
11*b*	—	5	,,	—	10	,,	$2N_2$	Same as No. 10.	Less strong deposit, darker than No. 10.
12	—	5	,,	—	10	,,	1Hg	White cloudiness, similar to No. 9.	White deposit.
13	1	—	0·172	5	—	0·029	$1N_1$	Yellowish cloudiness.	Dirty yellow deposit, whitish upper layer.
14	1	—	,,	5	—	,,	$1N_2$	Whitish cloudiness.	Yellowish deposit.
15	—	1	,,	5	—	,,	$1N_1$	Brownish yellow cloudiness.	Brownish yellow deposit, upper layer pale yellow.
16	—	1	,,	5	—	,,	$1N_2$	Whitish cloudiness.	Whitish deposit.
17	—	1	,,	4	1	,,	$1N_1$	Brownish yellow cloudiness.	Greyish deposit, upper layer yellowish.
18	—	1	,,	4	1	,,	$1N_2$	Yellowish cloudiness.	Greyish deposit, upper layer yellowish.
19	—	1	,,	3	2	,,	$1N_1$	Clear brown precipitate.	Light brown deposit, upper layer yellowish.
20	—	1	,,	3	2	,,	$1N_2$	Brownish yellow cloudiness.	Brownish yellow deposit, upper layer yellowish.
21	—	1	,,	2	3	,,	$1N_1$	Clear brown precipitate.	Greyish brown deposit, upper layer yellowish.
22	—	1	,,	2	3	,,	$1N_2$	Strong light brown cloudiness.	Light brown deposit, upper layer yellow.
23	—	1	,,	1	4	,,	$1N_1$	Brown precipitate.	Reddish brown deposit, upper layer yellow.
24	—	1	,,	1	4	,,	$1N_2$	Brown precip., slower.	Reddish brown deposit, upper layer yellow.
25	—	1	,,	—	5	,,	$1N_1$	Normal reaction, translucent liquid, intense brown.	Reddish brown deposit.
26	—	1	,,	—	5	,,	$1N_2$	Ditto ditto	Reddish brown deposit.
27	—	1	,,	—	5	,,	$2N_2$	Same appearance as No. 26.	Reddish brown deposit.
28	1	—	,,	5	—	,,	$2N_2$	Same appearance as No. 14.	Whitish deposit, like No. 14.
29	—	—	0·000	5	—	0·000	$1N_1$	Slight white cloudiness.	Slight whitish deposit.

(*a*) N_1 = Nessler's solution, 1st formula.
N_2 = ,, ,, 2nd ,,
Hg = 2 per cent aqueous solution of mercuric chloride.

recourse to Nessler's solution, this reagent gives, above all if prepared according to the formula preferred by M. Neumann, neither colouration nor brown precipitate. They further show (Nos. 13 to 26) that the normal action of Nessler's solution shows itself so much the less as the proportion of alcohol increases, and that even one-sixth of alcohol suffices to considerably modify the appearance of the mercuric precipitate.

Experiments Nos. 27 and 28 prove that the quantity of reagent employed in the preceding experiments is sufficient; No. 29 that Nessler's solution is clouded by *commercial* absolute alcohol. I am inclined to believe that this cloudiness would not be produced if the alcohol were *chemically pure*.

Thus, as I have already said (*Zeit. f. Anal. Chemie, loc. cit.*), mercuric chloride reacts with ammonia, as well in

an alcoholic solution as in an aqueous solution; but that the reaction is *considerably less sensitive*, with an equal quantity of ammonia, than the normal reaction of Nessler's solution.

ON A PROPERTY OF THE LINES AND BANDS IN ABSORPTION SPECTRA.

By Dr. G. B. RIZZO.

GASEOUS bodies present in general a line-spectrum, liquids a band- or a continuous spectrum, and solids a continuous spectrum; and it is admitted that this property is due to the different freedom of movement, or to the different complexity of the molecules in the three states of aggregation.

Besides, in each of these states the spectra of substances depend on their physical condition. Gases in particular can give a line spectrum or also a band spectrum, according to their temperature and the manner in which they are excited by electricity. This is clearly demonstrated by the researches of Plücker, Hittorf, Mitscherlich, Angström, Wüllner, Schuster, Lockyer, Ciamician, and others.

But whilst former experimentalists have considered this variability of the spectra as a simple and direct consequence of variation in the physical conditions of the bodies, Angström contends that it is to be ascribed to the formation of particular groupings of molecules which will be like different allotropic states of one and the same body. The question cannot be said to be as yet fully solved, and it is very important both in itself and for its application in the spectral analysis of the celestial bodies.

The main difficulty which presents itself in the study of the variability of the spectra is this:—We have no certain means of knowing the molecular exchanges which occur in incandescent bodies when raised to those elevated temperatures at which the spectra are modified. For this reason it is more convenient to study the variations presented by the absorption spectra of the bodies when they are heated between such intervals of temperature in which there do not occur changes in their chemical constitution.

Wishing to study the property of spectral lines and bands, I have found it very necessary to observe what bodies and which of their absorption spectra present a totality of lines and bands.

Such bodies are not very numerous, and some of them cannot be of service in this study because they are readily subject to chemical alteration, or leave room for such uncertainty concerning their constitution, as occurs in the salts of didymium, which present in their absorption spectrum a wonderful complex of lines and bands, and seeming to be a mixture of various other bodies endowed with different optical properties. Chromium oxalate forms with the alkaline metals, and also with iron, a series of double salts of a fine red colour which have a well-defined line. Among these the double oxalate of chromium and potassium is important, which is also known as Brewster's salt, because he diligently studied it, thinking that the optical property of this salt would be a decisive proof in favour of the emission theory of light.

The spectrum of Brewster's salt dissolved in glycerin at the ordinary temperature is formed of three very distinct bands—one in the red, ending in $\lambda=715\ \mu\mu$; the second extends between $\lambda=665$ and $\lambda=505$; and the last begins at $\lambda 478$. Between the two former bands there is a distinctly defined line at $\lambda=704\ \mu\mu$. I have proposed to study the property of this line, and of the bands with the variation of the temperature of the oxalate.

The salt is dissolved in glycerin by heating it to a slightly elevated temperature, but it is known that the absorption spectrum of the solution in glycerin is similar to that of the aqueous solution. The heating apparatus is composed of a hollow cylinder of brass with two walls, between which circulates the steam generated in a small boiler, as in the heating apparatus of Regnault's calorimeter. The solution to be studied is placed in one of those ordinary glass recipients with its opposite faces parallel, which are commonly used for the study of the absorption spectra of liquids, and it is supported in the middle of the central cavity of the cylinder, which is closed at both ends with two corks. The light of an Auer's lamp passes through the solution, passing through a slit made in the side of the cylinder and closed by two parallel plates of glass. The absorption spectrum was determined with the universal spectroscope of Krüss, fitted with a simple prism of heavy flint glass, and containing the solution at 16° and then at the temperatures of 98°, 130°, and 180°, obtained by heating with the steam of water, of amylic alcohol, and of aniline.

With the change of temperature the absorption-spectrum varies notably, and in the following table are indicated the wave-lengths of the principal bands of the spectrum in different conditions:—

Regions of the spectrum.	16°.	98°.	130°.	180°.
End of first band ..	715 $\mu\mu$	720 $\mu\mu$	724 $\mu\mu$	728 $\mu\mu$
Line of absorption ..	704	704	704	704
Beginning of second band..	665	669	671	672
Maximum intensity ..	590	596	600	604
End	505	515	521	526
Beginning of third band..	478	479	481	482

Besides the bands and the lines indicated there are also observed at the ordinary temperature (and most distinctly in the aqueous solution) a slight cloudiness at $\lambda = 702$, and another, first of the second band, between $\lambda=675$ and $\lambda=671$, but ceasing entirely to be visible when the temperature borders on 100°.

All the absorption-spectrum resumes its primitive appearance when the substance has cooled, and undergoes anew the same modifications when it is heated afresh. It may be therefore concluded that the absorption bands of the double potassium and chromium oxalate with an increase of temperature remove towards the less refrangible part of the spectrum, whilst in that part the intensity of some bands increases which are not visible at lower temperatures, whilst the line preserves its position unaltered.

By the interpretation of this phenomena I have aided in recording the principles commonly admitted concerning the constitution of bodies. This is considered as so many aggregates of small material particles, molecules, which may be variously grouped some to others, and are composed of smaller particles physically inseparable, that is, atoms.

The component molecules and atoms are in continuous movement, and the energy of the motions of translation of the molecules determines their absolute temperature.

If it is admitted that both the continuous light of the spectra of solids and liquids and the luminous zones of the band spectra, and the light of the line spectra are produced by the sole movements of the molecules and the atoms, the study of the luminous spectra is reduced to a study of such movements. But there are some phenomena not so easily explained by setting out from this last hypothesis, and therefore it is now sought to explain the nature of the luminous energy by setting out from the postulates of the electro-magnetic theory.

Without framing any hypothesis on the nature of the luminous phenomena, it may be said that the lines of the bands of the absorption spectrum have a distinct origin, since they behave differently with the changes of the physical conditions of the bodies which produce them; and since the position of the bands appear more strictly connected with the temperature of the bodies, as well as with the molecular movements, it may be said that the

lines have their origin in the atoms, and the bands in the molecules of bodies.—*Il Nuovo Cimento.*

THE METHODS OF SUGAR ANALYSIS.*

(Continued from p. 214).

Reducing Sugars (continued).

(*c*) *Gravimetric Method for Materials Containing 1 per cent or Less of Invert Sugar.*—The solution of the material to be examined is so prepared as to contain 20 grms. in 100 c.c., and it must be freed from suspended impurities by filtration through paper or by use of lead acetate, removing the excess of lead by means of sodium carbonate. In a beaker of 250 c.c. capacity place 50 c.c. of the mixed copper reagent and 50 c.c. of the sugar solution. Heat this mixture at such a rate that approximately four minutes are required to bring it to the boiling-point, and boil for exactly two minutes. Add 100 c.c. of cold, recently boiled, distilled water. Filter immediately through a weighed filtering tube of hard glass under pressure. The asbestos film in the filtering tube is supported by a perforated disk or cone of platinum, and should be washed free from loose fibres before weighing and moistened previous to the filtration. The tube is provided with a detachable funnel during the filtration so that none of the precipitate accumulates near the top, where it could be removed by the cork used during the reduction of the cuprous oxide. The precipitate is all transferred to the filter and thoroughly washed with hot water, following the water by alcohol and ether successively. After being dried the tube is connected with an apparatus for supplying a continuous current of dry hydrogen, gently heated until the cuprous oxide is completely reduced to the metallic state, cooled in the current of hydrogen, and weighed. The increase in weight is the weight of copper reduced by 10 grms. of the sample. The corresponding percentage of invert sugar is found by use of the following Table:—

Herzfeld's Table for the Determination of Invert Sugar in Materials Containing 1 per cent or Less of Invert Sugar.†

Copper reduced by 10 grms. of material.	Invert sugar.	Copper reduced by 10 grms. of material.	Invert sugar.
M.grms.	Per cent.	M.grms.	Per cent.
50	0·05	150	0·56
55	0·07	155	0·59
60	0·09	160	0·62
65	0·11	165	0·65
70	0·14	170	0·68
75	0·16	175	0·71
80	0·19	180	0·74
85	0·21	185	0·76
90	0·24	190	0·79
95	0·27	195	0·82
100	0·30	200	0·85
105	0·32	205	0·88
110	0·35	210	0·90
115	0·38	215	0·93
120	0·40	220	0·96
125	0·43	225	0·99
130	0·45	230	1·02
135	0·48	235	1·05
140	0·51	240	1·07
145	0·53	245	1·10

The weight of copper may be obtained as follows:—The filtration after reduction is made in a Gooch crucible, and the beaker and precipitate thoroughly washed with hot water without any effort to transfer the precipitate to the filter. Wash the asbestos film and the adhering cuprous oxide into the beaker by means of a wash bottle containing hot dilute nitric acid. After the copper is all in solution, re-filter through a Gooch crucible with a thin film of asbestos, and wash thoroughly with hot water. Add 10 c.c. of dilute sulphuric acid (containing 200 c.c. of sulphuric acid—specific gravity 1·84—per litre), and evaporate the filtrate on the steam-bath until the copper salt has largely crystallised out. Heat carefully on a hot plate or over a piece of asbestos board until the evolution of white fumes shows that the excess of nitric acid is removed. Add 8 to 10 drops of nitric acid (specific gravity 1·42), and rinse into a platinum dish of 100 to 125 c.c. capacity. Precipitate the copper by electrolysis. Wash with water thoroughly before breaking the current, remove the dish from the circuit, wash with alcohol and ether successively, dry at a temperature that can be borne by the hand, and weigh. The evaporation of the liquid for the removal of the excess of nitric acid may be avoided by the following process:—Transfer the asbestos film from the crucible to the beaker by means of a glass rod, and rinse the crucible with about 30 c.c. of a boiling mixture of dilute nitric and sulphuric acids, containing 65 c.c. of sulphuric acid (specific gravity 1·84) and 50 c.c. of nitric acid (specific gravity 1·42) per litre; or the asbestos film with the adhering cuprous oxide may be treated by the method of Formanek given below by transferring to the beaker containing the rest of the suboxide and washing the crucible with 2 to 4 c.c. of nitric acid (strong) to remove all adhering precipitate, receiving the solutions in the beaker. The crucible is then washed with 5 to 10 c.c. water, which is also received in the beaker. After all the cuprous oxide in the beaker is dissolved, the crucible is worked with an additional quantity of water. Re-filter through a Gooch crucible and wash thoroughly with hot water, limiting the volume of the filtrate to 75 to 80 c.c. Transfer to a platinum dish and electrolyse as described above. Wash before interrupting the current, using water acidulated with sulphuric acid at first.

(*d*) *Gravimetric Method for Materials Containing More than 1 per cent of Invert Sugar.*—Prepare a solution of the material to be examined in such a manner that it contains 20 grms. in 100 c.c. after clarification and the removal of the excess of lead. Prepare a series of solutions in large test-tubes by adding 1, 2, 3, 4, 5, &c., c.c. of this solution to each successively. Add 5 c.c. of the mixed copper reagent to each, heat to boiling, boil two minutes, and filter. Note the volume of sugar solution which gives the filtrate lightest in tint, but still distinctly blue. Place twenty times this volume of the sugar solution in a 100 c.c. flask, dilute to the mark, and mix well. Use 50 c.c. of the solution for the determination, which is conducted as described under *c*, until the weight of copper is obtained. For the calculation of the result use the following formulæ and table of factors of Meissl and Hiller:—

Let Cu = the weight of copper obtained;
P = the polarisation of the sample;
W = the weight of the sample in the 50 c.c. of the solution used for determination;
F = the factor obtained from the table for conversion of copper to invert sugar;

$\frac{Cu}{2}$ = approximate absolute weight of invert sugar = Z;

$Z \times \frac{100}{W}$ = approximate per cent of invert sugar = y;

$\frac{100\,P}{P+y}$ = R, relative number for sucrose;

100 − R = I, relative number for invert sugar

$\frac{Cu\,F}{W}$ = per cent of invert sugar.

* Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (American) at its Meeting at Chicago, August, 1893.

† *Zeitschrift des Vereins fur die Rübenzucker-Industrie des Deutschen Reichs*, 1885, xxxv., 967.

Z facilitates reading the vertical columns; and the ratio of R to I, the horizontal columns of the table, for the purpose of finding the factor (F) for calculation of copper to invert sugar.

Example: The polarisation of a sugar is 86·4, and 3·256 grms. of it (W) are equivalent to 0·290 grm. of copper. Then—

$$\frac{Cu}{2}=\frac{0{\cdot}290}{2}=0{\cdot}145=Z$$

$$Z\times\frac{100}{W}=0{\cdot}145\times\frac{100}{3{\cdot}256}=4{\cdot}45=Y$$

$$\frac{100\,P}{P+y}=\frac{8640}{86{\cdot}4+4{\cdot}45}=95{\cdot}1=R$$

$$100-R=100-95{\cdot}1=I=4{\cdot}9$$

$$R:I=95{\cdot}1:4{\cdot}9$$

By consulting the Table it will be seen that the vertical column headed 150 is nearest to Z, 145, and the horizontal column headed 95 : 5 is nearest to the ratio of R to I, 95·1 : 4·9. Where these columns meet we find the factor 51·2, which enters into the final calculation—

$$\frac{Cu\,F}{W}=\frac{0{\cdot}290\times51{\cdot}2}{3{\cdot}256}=4{\cdot}56 \text{ per cent of invert sugar.}$$

Meissl and Hiller's Factors for the Determination of More than 1 per cent of Invert Sugar.*

Approximate absolute weight of invert sugar = *Z*.

Ratio of sucrose to invert sugar = R : I.	200 m.grms.	175 m.grms.	150 m.grms.	125 m.grms.	100 m.grms.	75 m.grms.	50 m.grms.
	P.c.	P.c.	P.c.	P.c.	P.c.	P.c.	P.c.
0 : 100	56·4	55·4	54·5	53·8	53·2	53·0	53·0
10 : 90	56·3	55·3	54·4	53·8	53·2	52·9	52·9
20 : 80	56·2	55·2	54·3	53·7	53·2	52·7	52·7
30 : 70	56·1	55·1	54·2	53·7	53·2	52·6	52·6
40 : 60	55·9	55·0	54·1	53·6	53·1	52·5	52·4
50 : 50	55·7	54·9	54·0	53·5	53·1	52·3	52·2
60 : 40	55·6	54·7	53·8	53·2	52·8	52·1	51·9
70 : 30	55·5	54·5	53·5	52·9	52·5	51·9	51·6
80 : 20	55·4	54·3	53·3	52·7	52·2	51·7	51·3
90 : 10	54·6	53·6	53·1	52·6	52·1	51·6	51·2
91 : 9	54·1	53·6	52·6	52·1	51·6	51·2	50·7
92 : 8	53·6	53·1	52·1	51·6	51·2	50·7	50·3
93 : 7	53·6	53·1	52·1	51·2	50·7	50·3	49·8
94 : 6	53·1	52·6	51·6	50·7	50·3	49·8	48·9
95 : 5	52·6	52·1	51·2	50·3	49·4	48·9	48·5
96 : 4	52·1	51·2	50·7	49·8	48·9	47·7	46·9
97 : 3	50·7	50·3	49·8	48·9	47·7	46·2	45·1
98 : 2	49·9	48·9	48·5	47·3	45·8	43·3	40·0
99 : 1	47·7	47·3	46·5	45·1	43·3	41·2	38·1

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 19th, 1894.

Dr. H. E. Armstrong, President, in the Chair.

Messrs. W. Lloyd Williams, R. Curling Styles, and J. Cardwell Quinn were formally admitted Fellows of the Society.

Certificates in favour of the following candidates were read for the first time:—George Donald, Arnold Print Works, North Adams, Mass., U.S.; Robert John Flintoff-Haxby, Crumpsall Lane, Crumpsall, Manchester; Sydney Walters Harris, 15, Lansdowne Terrace, Walters Road Swansea; J. H. Hickens, North Devon Lodge, Cheltenham; Wilmot Holt, jun., The Park, Didsbury, Manchester; Arthur Peach Hope, Salisbury Road, Leicester; James McLeod, 2, Gladstone Terrace, Paisley; E. Brooke Pike, 6, Lathom Road, East Ham; Herbert Stephen Shorthouse, 47, Pershore Road, Birmingham; Ernest Alfred Smith, 17, Oval Road, Regent's Park, N.W.; Herbert W. Steel, Wedderburn, Paisley; Edward B. Shuttleworth, Trinity Medical College, Toronto; George Dupré Thudichum, Montrose, Dorset Road, Merton Park; Robert Wright, 11, Eagle Parade, Buxton.

Of the following papers those marked * were read:—

*132. "*The Magnetic Rotations of Derivatives of Fatty Acids containing Halogens; of Acetic and Propionic Acids, Phosgene, and Ethylic Carbonate.*" By W. H. Perkin, Ph.D., F.R.S.

The first subject considered in the paper is the magnetic rotation of acetic and propionic acids in reference to their molecular complexity. From the determinations made at widely different temperatures it is considered that the kind of association of molecules referred to by Ramsay and Shields does not influence the results. In the cases of phosgene, ethylic chloroformate, and ethylic carbonate it is shown that the two chlorine atoms in phosgene behave as if they had two different values; that in such derivatives as ethylic chloroformate, for example, having the smaller value. On comparing this compound with phosgene and ethylic carbonate, it would appear that the two ethoxyl groups in this latter substance which displace the two chlorine atoms in phosgene, also have two separate values. The next section relates to the chloro- and bromo-derivatives of acetic acid and its ethereal salts. With respect to the acids it is found that alone or in aqueous solution they yield practically the same numbers. The effect of etherification on these acids, however, is found to be anomalous. Instead of changing in rotation by the same amount as in the case of acetic acid and its ethereal salts, the values for ethyl and methyl increase as the number of halogen atoms introduced. There is one exception, viz., dibromacetic acid. The alteration of the rotation of acetic acid and its ethereal salts by the introduction of chlorine is then considered. It is shown that differences corresponding to successive displacements in the case of chlorine do not follow a regular order; but, with bromine, they generally increase with the displacements, and the fluctuations are shown to be similar in character to those exhibited by chlorine and bromine derivatives of methane. Ethylic iodoacetate was found to give lower results for iodine than propyl iodide. The rotation of ethylic α-chloro-propionate furnishes a value for chlorine similar to that in ethylic dichloracetate. Ethylic trichlorlactate gives an average value for chlorine somewhat lower than that of ethylic trichloracetate.

The measurements of α-bromopropionic acid and butyric acids and their ethereal salts furnished the usual rotations for members of a homologous series for the same difference of composition; the usual value being obtained for a difference of CH_2, and also for bromine. In the acids, however, the value is apparently smaller than in the ethereal salts, as these, like the acetic compounds, are changed by etherification more than the compounds not containing halogens.

The difference in the values obtained for the chlorine and bromine compounds are then considered, and suggestions are made as to special circumstances which may influence the magnetic rotation.

Discussion.

The President remarked that Dr. Perkin's results afforded further evidence of the remarkable influence of *several* halogen atoms to which Thomsen had first specially called attention in his thermochemical researches. The very noteworthy difference between the magnetic constants of the chlorinated and brominated acids to which Dr. Perkin drew attention, which was correlated

* *Zeitschrift des Vereins fur der Rubenzucker-Industrie des Deutschen Reichs*, 1889, xxxix., 735.

with an equally striking difference manifest on comparing the boiling-points, served to suggest that the method of reducing the results was scarcely such as to bring out the true magnetic constants.

Dr. GLADSTONE commented on the irregularities in the values obtained for the chloro-derivatives of acetic acid as compared with the corresponding bromo-derivatives.

Mr. RODGER supported the President's statement that the character of Dr. Perkin's results no doubt depended to some extent on the mode of treating the experimentally observed quantities. In measurements where the wave-length of the light and the strength of the magnetic field remained the same throughout, the difficulty lay in obtaining a measure of the molecular rotation in which the influence of temperature on the rotatory power was either eliminated or allowed for. Dr. Perkin employed the ratio $\alpha M/d$ as determined for the substance to the corresponding quantity in the case of water as the value of the molecular rotation. This ratio would only be independent of the temperature if α/d were the same function of the temperature for water and for the substance. The early experiments of De la Rive, Dr. Perkin's own results, as well as observations as yet unpublished by Mr. Watson and the speaker, have shown that this is not the case.

Recently, Guye has proposed the expression—

$$\alpha\sqrt[3]{M/d}$$

instead of $\alpha M/d$ as a more probable measure of the molecular rotation. At first sight (compare *Proc. C. S.*, 1893, 236) this new expression appears to be the more satisfactory. It may be shown, however, that it can only give the correct measure of the molecular rotation if it is assumed that the medium consists of elementary cubes at the centre of each of which is a molecule, and the volume of each of which is proportional to the molecular volume. We should then regard each cube as representing the sphere of activity of the molecule, and consider that the total effect of the medium depends solely on the number of cubes which the ray traverses. Whichever measure be adopted, experiment shows that neither eliminates the effect of temperature, neither α/d nor— .

$$\alpha\sqrt[3]{d}$$

is constant; hence satisfactory conclusions can only be arrived at when the effect of temperature on magnetic rotation has been more fully studied and values of the molecular rotation have been measured at comparable temperatures.

In the communication under discussion, Dr. Perkin has furnished extensive support to the conclusion that the effect on a physical property brought about by replacing an atom of hydrogen in a methyl group by an atom of halogen varies according as it is the first, second, or third halogen atom which is thus united to the carbon atom. In their paper on viscosity (shortly to appear in the *Phil. Trans.*), Professor Thorpe and the speaker pointed out that in the case of viscosity, surface-energy, boiling-point, and critical temperature, the change produced on replacing the first hydrogen atom was the greatest, and that on replacing the third hydrogen atom the smallest; whereas, in the case of molecular volume and molecular refraction, the reverse rule appeared to hold. The properties in the first group depend mainly on effects in play between molecules; the last two properties, on the other hand, are mainly the result of influences resident within the molecules. The sense in which the effect of substitution changed thus appeared to be correlated with the nature of the property dealt with. Dr. Perkin's present results show, however, that in the case of the same property the substitution effect may vary in both senses, or the variation may even be irregular. Whether this result, as well as the other anomalies observed by Dr. Perkin, are due to the fact that the effect of temperature is not allowed for, or whether it is also due to the fact that the molecular complexity of some of the liquids examined influences the results, can only be decided when more is known regarding the mode in which the molecular rotations should be calculated, and when the effect of change of density has been more fully investigated.

Dr. PERKIN remarked that the effect of temperature on magnetic rotations, to which he had often drawn attention, is usually small with fatty compounds, although more considerable in the aromatic series.

In closing the discussion, the PRESIDENT added that the impression he had gained from Dr. Perkin's figures was that in order to take into account the diverse nature of the chlorinated and brominated acids, it was probably necessary to introduce a term into the calculation which would give expression to the fact that whereas there was a great difference in boiling-point between the di- and tribromo-derivatives, there was but a slight one between the corresponding chlorinated compounds.

*133. "*The Action of Concentrated Acids on certain Metals when in Contact with each other.*" By GEORGE J. BURCH, M.A., and J. W. DODGSON.

In 1790, James Keir (*Phil. Trans.*, 1790, p. 367) announced that a mixture of strong nitric and sulphuric acids could be used for stripping the silver from old-plated copper goods. The authors have investigated the chemical and electrical phenomena of this and other reactions of the same type, and now present a preliminary account of their work.

Experiments with a Silver-copper Couple.—A sheet of "pure" silver was cut into strips, which were scraped bright, bent into a U-shape, and weighed. To each was fitted a similar strip of copper, carefully cleaned and weighed, the whole forming an elliptical ring, held together by the elasticity of the metals. A number of test-tubes arranged in a water-bath contained the mixed acids diluted with various proportions of water. Each ring remained under the surface for forty-seven minutes, and was then rapidly removed, wiped, washed, and weighed. The liquid was not stirred during the experiment.

In the stronger solutions, a yellowish white powder separates from the silver, and a clear heavy liquid of strong refracting power streams from it. Little or no gas is evolved.

During a few seconds after immersion the copper is covered with a white froth. This clears away, and the surface remains bright. Probably nearly all the loss of copper occurs at this stage. The liquid becomes of a pale greenish yellow colour, and a good deal of an almost white powder is deposited. A blue tint only appears when six or more molecular proportions of water are present to one of sulphuric acid. When the dilution is represented by $8H_2O+H_2SO_4$, nitrous fumes first begin to appear. It will be observed that the amount of silver dissolved is least with $5H_2O$, after which it increases again, and that the copper, which is practically untouched at $3H_2O$, is now rapidly attacked. At temperatures above 50° C. the results are somewhat different.

Magnesium-Silver Couple.—In a mixture of 10 parts sulphuric acid of rel. dens. 1·84 with 1 part nitric acid of sp. gr. 1·436, the magnesium retained its brilliant appearance during an hour and twenty minutes, while the silver dissolved steadily. No gas was evolved. The magnesium lost 0·0015 grm., and the silver lost 0·1167 grm., the ratio of the loss per unit area being Ag : Mg :: 61·5 : 1.

Electrical Phenomena.—The difference of potential between two metals in concentrated acids cannot be measured with the quadrant electrometer in the ordinary way, because in certain cases the chemical changes are different according as the circuit is closed or open. The influence of each metal on the rate of solution of the other is in most cases strongly marked. With the copper-silver couple the resistance increases rapidly on short circuit, apparently at the surface of the copper. The quantity of current is not proportional to the weight of silver dissolved. This part of the subject will be dealt with in a future paper.

Silver-Copper Couple, in a Mixture of 1 part Nitric Acid of rel. dens. 1·436 with 5 parts H_2SO_4 of rel. dens. 1·84 with various proportions of Water ranging from 1 to 10 molecules per molecule of H_2SO_4. Temperature 20° C.

Molecular proportions of water.	Silver.			Copper.		
	Taken.	Loss.	Loss.	Per unit area.	Loss.	Taken.
None added	0·7710	0·0426	0·01075	0·00027	0·0013	1·3265
1	0·7000	0·0358	0·00994	0·00061	0·0027	1·2082
2	0·7114	0·0234	0·00616	0·00038	0·0018	1·1320
3	0·7284	0·0251	0·00633	0·00075	0·0036	1·3252
4	0·7395	0·0170	0·00523	0·00250	0·0100	1·1954
5	0·7052	0·0052	0·00144	0·00288	0·0127	1·2209
6	0·7505	0·0110	0·00399	0·01792	0·0717	1·2671
7	0·7290	0·0176	0·00463	0·03475	0·1526	0·9775
8	0·7033	0·0343	0·00866	0·05116	0·2456	1·3216
9	0·6957	0·0268	0·00827	0·05302	0·2129	1·1854
10	0·6342	0·0300	0·00833	0·05895	0·2594	1·2055

Sodium and Sulphuric Acid (rel. dens. 1·84).—A freshly-cut cube of sodium, about 5 m.m. each way, impaled on the end of a strip of the metal used, was dropped into a test-tube containing about 15 c.c. of the acid, the tube being immersed in a jar of water (16°), the mouth of which was inclined away from the operator. As a further precaution a glass screen was used. The initial action was in most cases over in less than five minutes. The results of the experiments may be summed up as follows:—

Sodium alone, weighted with a glass rod to sink it, was less rapidly attacked by strong sulphuric acid at 16° C. than by water. The action was moderate but steady. Bubbles of gas were freely given off, and very little heat was evolved. The sodium was completely dissolved in about twenty minutes, a small quantity of a whitish substance being formed near it towards the end of the process.

The contact of another metal with sodium exerts an influence on the rate and manner of its solution in strong sulphuric acid. In most cases the action of the solvent is much retarded. The gas evolved comes from the *entire surface* of the platinum, carbon, or iron, when these substances are employed, and is given off freely from first to last. No bubbles appear on the sodium, which is clean and bright. The iron-sodium couple lasted forty minutes, the platinum-sodium about two hours, and the carbon-sodium was still acting slowly after eight hours. In this case gas came from the sodium, and none from the carbon for the first ten minutes after the initial effervescence was over. Then the sodium became quiescent, and bubbles rose from the carbon. Sulphur was separated after a while.

With lead and tin the action was similar, but much slower. The sodium was not so clean and the liquor became very turbid.

The tin acquired a brownish yellow coating and the lead assumed a grey colour. It was several days before the sodium disappeared.

Zinc exerts comparatively little restraining action, but makes a very turbid solution.

An aluminium-sodium couple, weighted with a glass rod to sink it, evolved torrents of gas, and after about five seconds the sodium caught fire.

A magnesium-sodium couple similarly weighted gave a flash of light as it touched the liquid. Then, for about three seconds, there was a copious evolution of gas, and the sodium burst into flame while completely submerged.

With the cadmium-sodium couple the action was extremely slow. Fewer bubbles came from the sodium than from the cadmium, which became covered with a brown film. The liquor was turbid.

Coming now to those metals which produce a markedly different effect.

Nickel scarcely evolves any gas, but is soon coated *near the sodium* with a brownish film, while a few bubbles rise from the sodium. Antimony exerts the most powerful restraining influence of any substance yet tried. The initial action is very small. Bismuth behaves in much the same way. Both these metals become coated with a film near the sodium. Very little gas is evolved, and what there is comes from the sodium, which remains for days undissolved.

Silver in contact with sodium turns dark. Very few bubbles appear on either metal, but the sodium, which is quite clean, is visibly smaller after two hours.

Thus, a magnesium-silver couple is almost inert in the acid, and a sodium-silver couple acts very slowly, but a magnesium-sodium couple bursts into flame, whereas either metal separately would be a long time in dissolving.

Copper evolves no gas, but becomes coated with the gas given off from the sodium, and presents a reddish fawn-coloured film. After an hour or so a secondary action sets in, apparently from the decomposition of some substance formed near the sodium; and those parts of the copper which remained bright are attacked, the production of an insoluble dark brown compound, rendering the liquid turbid. The sodium is brilliantly clean, and during the first stage of the reaction evolves gas slowly. This gas has no perceptible smell, but turns paper moistened with iodate of potassium and starch solution faintly blue after a while. The acid liquid does not bleach litmus or indigo, and gives no precipitate, and only a slight brown colouration on boiling, with nitrate of silver. Iodine is only slightly decolourised by it, and it is not affected by permanganate to a greater extent than the fresh acid. The turbid liquid gives off sulphur dioxide on heating.

*134. "*The Action of Light on Oxalic Acid.*" By A. Richardson.

Downes and Blunt, in 1879, observed that solutions of oxalic acid evolve carbon dioxide when exposed to light. In the present paper the author shows that hydrogen peroxide is also formed. Experiments are described in which this was found to be the case with numerous specimens of oxalic acid obtained from different sources, and carefully purified. The presence of the peroxide was proved by the titanic acid and chromic acid tests.

The decomposition of the acid was further studied in order to determine whether complete oxidation of the carbon to carbon dioxide occurred, or whether products of partial oxidation were also formed. The results of experiments in which the carbon dioxide evolved during the decomposition of a known weight of acid was estimated, showed that the oxidation of the carbon was complete.

The absence of intermediate products of oxidation seem to indicate that the formation of the peroxide is the direct result of the oxidation of the hydrogen of the acid, and is not brought about by secondary changes.

Experiments were also made in order to observe the influence of the concentration of the acid on the formation of the peroxide. The results obtained showed that while the total amount of hydrogen peroxide formed in the solution increased with the concentration of the acid, the proportion of peroxide formed to acid decomposed simultaneously decreased. The author draws the following conclusions:—

(1) Hydrogen peroxide is stable in solutions of oxalic acid in the dark.

(2) It is fairly stable in these solutions when exposed to light if excess of oxygen is present,

(3) Rapid decomposition of hydrogen peroxide occurs in solution of oxalic acid in absence of oxygen when their solutions are exposed to light.

*135. "*English Jute Fibre.*" By A. PEARS, jun.

In continuation of previous observations (*Trans.*, 1893), the seed saved from the plants grown in 1892 was sown at two periods, March and June, 1893. Parallel with these, cultivations were made from Indian seed. The plants were cut down in the late autumn when the seed is mature, and the four specimens of fibre obtained were compared.

Slight differences were observed in the resistance to hydrolysis and in the percentages of cellulose, the specimens from the early sowings being the better.

One specimen from the English seed (1892) contained 43 per cent of carbon and 6 per cent of hydrogen. It furnished 8·5 per cent of furfural (calculated on the fibre), and absorbed 15 per cent of chlorine.

The two last numbers are similar to those obtained with the normal fibre—whereas the composition shows an important divergence in the percentage of carbon, the normal percentage being 46·5.

It is evident, therefore, from the study of these artificial cultivations, that they exhibit the essential features of jute fibre, and differ chiefly in the degree of hydration, which is dependent on the conditions of growth. The specimen may in fact be regarded as a hydrated modification of the normal fibre, with which it corresponds in all the characteristic properties, differing merely in external features (colour, softness, &c.).

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, April 27th, 1894.

Prof. A. W. RÜCKER, M.A., F.R.S., President, in the Chair.

A PAPER "*On the Mechanism of Electrical Conduction. Part I. Conduction in Metals,*" was read by C. V. BURTON, D.Sc.

Considering a body not at absolute zero of temperature, the author shows that electromagnetic radiation would result in heat being degraded into a lower form of energy if any parts of finite electric conductivity were present, and from the fact that our planet is not devoid of heat, deduces the following:—

Theorem I. "In a region containing matter there may be (and probably always are) some parts which are perfect insulators and some parts which are perfect conductors, but there can be no parts whose conductivity is finite—unless every finitely conductive portion is enclosed by a perfectly conductive envelope." This conclusion is in accordance with Poisson's theory of dielectrics and with Ampère's and Weber's theories of magnetism and diamagnetism respectively.

Theorem II. is enunciated as follows:—"In metals, and in other non-electrolytes whose conductivity is finite, the transmission of currents must be effected by the intermittent contact of perfectly conductive particles"; and as a corollary Theorem III. is given: "If we suppose that a substance at the absolute zero of temperature there is no relative motion amongst the molecules or amongst their appreciable parts, it follows that every substance at this temperature must have either infinite specific resistance (which does not imply infinite dielectric strength) or infinite conductivity." Fleming and Dewar's experiments on pure metals tend to confirm this.

The author then shows why, on the intermittent contact hypothesis, a conductor is heated when a current flows throughout. On the assumption that in ordinary conductors the relation between the electromotive intensity in the intermolecular spaces and electric displacement is a linear one, and that the electric forces are small in comparison with the ordinary intermolecular forces, Ohm's law is deduced.

A model is next described, by means of which contact E.M.F. and the Peltier effect can be represented and explained; and in considering Volta E.M.F.'s the author points out that it is doubtful whether experiments in a perfect vacuum could decide the questions at issue in the contact-force controversy. The fact that the transparency of metals is much greater than Maxwell's theory indicates might be explained without attributing any new properties to the electromagnetic field by supposing the dimensions of molecules not quite negligible in comparison with the wave-length of light.

Prof. S. P. THOMPSON thought the paper had an important bearing on the kinetic theory of solids. He saw no reason why Ohm's law should be proved, for he regarded it as a definition.

The PRESIDENT said the author represented all actions as being due to collisions, thereby introducing the same difficulties as were felt in the kinetic theory of gases, viz., that collisions would give rise to mechanical oscillations in the molecules of shriller and shriller pitch. Prof. J. J. Thomson had recently given an explanation of electrical phenomena by vortex filaments.

After some remarks on the visibility of molecules by Mr. HOVENDEN,

Dr. BURTON, in reply to Prof. Thompson, said Ohm's law, when expressed as—

$$\frac{E}{C} = a\ constant,$$

was really a law, and not a mere definition.

A communication "*On the Design and Winding Alternate Current Electromagnets,*" by SILVANUS P. THOMPSON, D.Sc., F.R.S., and MILES WALKER, was read by the former.

The paper describes experiments showing that when the magnetic induction does not exceed 4000 (C.G.S.), the pull excited by a laminated electromagnet on its armature is the same whether it is excited by a continuous or by an alternating current of equal strength. For higher inductions the continuous current gives slightly greater force. Another experiment, made with selenoids and the U-shaped plunger of a Brush alternate current arc lamp, gave similar results.

In considering the question of winding alternate current electromagnets so as to obtain a given excitation when the current is supplied at constant voltage, it is shown that the ampère turns are inversely proportional to the number of turns, for the impedance varies nearly as the square of the number of turns. One important property of such electromagnets when supplied at constant voltage is that they give a fairly constant pull over a long range, for as the armature moves away from the magnet the current increases, thus counteracting to some extent the effect of distance. On the other hand, the alternating voltage required to obtain a given force is much greater than that needed with continuous currents. With the armature in contact with the core, the ratio of the two voltages was found to be 170, whilst separating them by 9·2 m.m. reduced the ratio to 21·5.

Prof. PERRY pointed out that the constant pull of the alternate current magnet followed immediately from the fundamental equation $e = rc + n\dot{I}$, where rc is small, for if e be constant then $\dot{I}$ and therefore I and I^2 are constant. He was interested to see that the pulls for equal ampère turns were the same, and indicated how the problem could be worked out mathematically when hysteresis was taken into account.

Mr. BLAKESLEY thought it better to fill the space on a

magnet full of copper rather than use wire only just large enough to carry the current, for the loss of energy would be reduced. Some of the formulæ given might be put in simpler form.

Mr. Swinburne said an alternate current magnet would only give constant pull in special cases. As another rule for winding alternate current magnets, he said, wind the magnets as for continuous currents, and put a condenser in to take the same current, thereby reducing the voltage required.

Mr. Blakesley said it would require a capacity of 600 microfarads to suit the magnet mentioned in the paper.

Dr. Thompson, in reply, agreed with Mr. Blakesley that the condenser was impracticable in many cases.

Major R. L. Hippisley, R.E., read a paper on "*A Graphical Method of Constructing the Curves of Current in Electromagnets and Transformers*," and exhibited a machine for drawing these curves.

Taking the ordinary equation for a simple alternate current circuit,—

$$E \sin pt - \frac{d B}{t d} = R i,$$

where B is the total magnetic flux and i the current, the author writes it in the form—

$$E \sin pt - m_k L \frac{di}{dt} = R i,$$

where L is the coefficient of self-induction of the circuit with the iron withdrawn, and m_k the tangent of the inclination of the B H curve at the point corresponding to the instant considered. This equation is integrated for a short part of the cycle, during which m may be considered constant, giving—

$$i = \frac{E}{R} \cos \theta_k \sin (pt - \theta_k) + A_k e^{\frac{-Rt}{m_k L}}.$$

Methods of finding the constants in the last equation are then described, and the method of drawing the current curves step by step explained. The machine for performing the process is illustrated in the paper, and the curve for an electromagnet fed with alternating current shown. The case of a transformer without magnetic leakage is worked out at some length, and the curves of primary and secondary current determined.

Dr. Sumpner said the author had used great care in working out a difficult problem more completely than usual. In cases such as arise in practice the R i term is small, and for this case Evershed showed how to determine the current curves of a transformer when the periodic state had been reached, some five or six years ago. He (Dr. Sumpner) had also shown how to graphically determine the current curves for circuits containing iron in 1888. The author's method was, however, of more general application.

Mr. Trotter enquired whether the machine could be used in practical alternate current problems, say, for example, to predetermine the E.M.F. curve of an alternator.

Major Hippisley replied to the points raised.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, May 7, 1894.

Sir James Crichton Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following Vice-Presidents for the ensuing year were announced:—Sir Frederick Abel, Bart., K.C.B., D.C.L., LL.D., F.R.S.; Sir Douglas Galton, K.C.B., D.C.L., LL.D., F.R.S.; William Huggins, D.C.L., LL.D., F.R.S.; Ludwig Mond, F.R.S.; Hugo Müller, Ph.D., F.R.S.; Basil Woodd Smith, F.R.A.S., F.S.A.; Sir James Crichton-Brown, M.D., LL.D., F.R.S., Treasurer; and Sir Frederick Bramwell, Bart., D.C.L., F.R.S., Hon. Secretary.

The following were elected Members of the Royal Institution:—The Rt. Hon. The Earl of Carnarvon; Alfred Henry Dawbarn; The Rt. Hon. George Denman; Edward J. Duveen; Richard E. Farrant; Henry Grinling; Bertram Keightley, M.A.; Mrs. Adelaide J. Moseley; F. W. Passmore, Ph.D.; Henry Rofe, M.Inst.C.E.; Miss Edith Woodd Smith; E. Viles; and The Hon. Sir Robert Samuel Wright, M.A.

The special thanks of the Members were returned for the following donations to the Fund for the Promotion of Experimental Research at Low Temperatures:—

Sir William O. Priestley, M.D.	£50
Sir David L. Salomons, Bart.	£50

NOTICES OF BOOKS.

Nature's Hygiene: a Systematic Manual of Natural Hygiene, containing also a detailed Account of the Chemistry and Hygiene of Eucalyptus, Pine, and Camphor Forests, and Industries connected therewith. By C. T. Kingzett, F.I.C., F.C.S. Fourth Edition. London: Baillière, Tindall, and Cox. 1894.

The present edition of this useful work differs from its predecessors chiefly in its more systematic arrangement, in an extension of the bacteriological matter, in the addition of a chapter on alimentation and foods, and of a discussion of the aërial oxidation of the turpentines and other essential oils.

To the eucalypti and the pines, the author has now added as sanitary agents the camphor trees, but otherwise his views on disinfection are substantially unchanged. That they are of very high value need not be questioned.

Like too many hygienists, however, Mr. Kingzett confines his attention too exclusively to the so-called zymotic diseases, which kill quickly, leaving the chronic maladies of debility, which may be transmitted to succeeding generations, unnoticed.

In the prefaces to the fourth and third editions we find utterances which deserve to be taken to heart and put in practice. Thus we read: "Chemical officers are urgently needed to act side by side with medical officers of health and engineers, to deal effectively with the many important matters affecting public health. . . . While the development of chemical science in recent years has been most marked, sanitary authorities have not sufficiently availed themselves of its services, but have relied much too confidently upon mere engineering skill. The disposal of the London sewage as at present effected will serve to exemplify my meaning, and may be taken by way of illustrating the disastrous results that may ensue from such an unfortunate reliance. The water carriage of sewage has grown in London from a blessing into an unmitigated and terribly costly evil."

Let us understand that the treatment of polluted waters, the admissibility of effluents into rivers, the eligibility of water supplies, &c., are *purely chemical questions.* An engineer may be at the same time a chemist and a biologist; so may a divine or a lawyer. But *merely as such*, even supposing that he had constructed a railway bridge across the Straits of Dover, he would be no more qualified to deal with the sewage question than would a clergyman for having delivered the most powerful sermons, or a lawyer for having successfully conducted the most sensational divorce or libel cases. Hence we cannot share Mr. Kingzett's charitable hope that the "possession of the Fellowship of the Institute of Chemistry may be accepted by the public as sufficient guarantee of the ability of its holders to satisfactorily discharge such duties!" Why the engineers who are are selected to deal with the treatment of sewage, &c., offer no guarantee at all! The

public has not doubted the competence of one or the other chemist to take up sanitary questions, but has ignorantly overlooked the fact that the questions are purely chemical, or chemico-biological. If we are not incorrectly informed, a very well known engineer is in the habit of asserting that crude untreated sewage is harmless, that perfectly purified sewage is harmless, but that anything intermediate is dangerous! Perhaps he may not be aware that pure water does not exist in nature.

The author speaks generally with knowledge and fairness of the various systems for the disposal of sewage. He fails, however, to condemn duly those processes which turn on the use of lime in any mixture. Such are the numerous patents obtained by Gen. Scott for precipitating sewage with lime and clay and converting the deposit into cement. By these processes the fertilising matter in the sewage is simply wasted, and the cement made has not, we understand, given any great satisfaction.

Mr. Bevan's scheme for conveying the London sewage to Foulness Island would be wasteful and costly, perhaps even more than the present plan of carrying the deposit down to the sea in barges. In sneering at "our boasted scientific knowledge," he overlooks the fact that "the useful parts of sewage" are already being "converted into a good practical manure," without the cost of channels extending from London to the Essex coast.

Sir J. B. Lawes's project of contentedly applying the London sewage as food for fishes can merely provoke a deep sigh.

As a whole, Mr. Kingzett's work may be welcomed as a valuable contribution to our sanitary knowledge.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 17, April 23, 1894.

Some Preliminary Remarks on the Mechanism of the Disassimilation of the Albumenoids and the Formation of Urea in the Economy. — Armand Gautier.—With the exception of urea and corresponding nitrogenous bodies directly eliminated in the urine, the products of the direct disintegration of the albumenoids of the protoplasms (glycogen, sugars, fats), are then submitted to oxidation. In the muscles the carbohydrates and the fats are destroyed by fermentation and oxidation. The fatty acids pass into the blood, and are there burnt by successive stages; but we may say that this second phase of disassimilation, a phase essentially oxidising, reaches only the products derived from the direct activity of the protoplasm, and takes place, so to speak, at the periphery of the cellule, and not in its essentially active protoplasmic part, which is almost everywhere reductive. I do not hesitate to affirm that in the liver and in other organs this fermentive and anaërobic splitting up of the albumenoids must be accompanied with the formation of very reductive and highly poisonous compounds (toxines, extractives, ptomaines, colouring matters), as experience shows, but even with the production of free hydrogen. Grehant has just announced that in his analyses of the normal blood of animals he has always found a certain quantity of free hydrogen, which has hitherto been confounded with nitrogen.

Sodium Ethylacetylacetate.—M. de Forcrand.—The author adopts the value +4·19 cal. for the hydratation heat of anhydrous sodium ethylacetylacetate, and consequently +4·39 cal. for its solution heat at +12 in 4 litres of water.

Detection of Abrastol in Wine.—L. Briand.—To 50 c.c. of wine put in a ½-litre phial the author adds 1 c.c. pure sulphuric acid, agitates, and introduces into the mixture 25 grms. of pure lead peroxide. After shaking energetically for five minutes it is thrown upon a filter moistened with water. He collects 40 c.c. of the filtrate, adds 1 c.c. of chloroform, and shakes again for a minute, when if the wine contained abrastol the chloroform takes up a yellow colouring matter. But with all natural wines the solvent remains perfectly colourless. If the yellow liquid from an abrastolised wine is evaporated, the residue, on treatment with a few drops of sulphuric acid, takes a splendid green colour.

Observations on M. Calmette's Paper on the Poison of Serpents.—C. Phisalix and G. Bertrand.—The authors claim priority in the announcement of the fact that the venom of vipers on exposure to heats of 75° to 80° possesses in aqueous solution vaccinating properties against the venom in its original state, and that the blood of animals thus immunised becomes capable of neutralising the effects of the original venom. M. Calmette appears to have re-published these results without reference to the authors.

Experimental Researches on the Place of the Formation of Urea in the Animal System. Preponderance of the Liver in this Formation.—M. Kaufmann.—The author shows that the formation of urea is not entirely confined to the liver, as all the tissues produce a certain quantity. Still the liver must be regarded as the most active focus of the production of urea in the animal when fasting. The production of urea seems thus at once connected to the phenomena of nutrition effected in the tissues, and to the phenomena of elaboration and of the preparation of nutrient materials poured into the blood by the hepatic gland.

Production of Glycosuria in Animals by Means of Psychical Influences.—Paul Gibier.—Certain of the lower animals, like man, may become affected with *diabetes mellitus* to a fatal extent by depressing emotions.

Contributions to the Study of the "Plague" of Fresh Waters.—E. Battaillon.—An epidemic is produced in fresh waters by a diploccus. It attacks fish, frogs, cray-fish, &c. Its spread is checked by aëration.

Bulletin de la Société Chimique de Paris. Series 3, Vols. xi.-xii., No. 5.

Apparatus for Fractionated Distillation.—Marius Otto.—This paper requires the accompanying figure.

A Comparison between the Coloured and the Colourless Compounds of Methane Twice or Three Times Phenylated.—A. Rosenstiehl.—Colourless leukaniline differs from coloured magenta by the substitution of an atom of hydrogen for an atom of chlorine. This condition does not, however, suffice. A decisive part belongs to the group (NH_2), which in magenta is found in the three phenylic groups.

Determination of Ammonia by the Calorimeter.—Lojos Ilosway de Nagy Iloswa.—The essential part of this memoir will be inserted in full.

Rapid Determination of the Xantho-uric Compounds in Urine.—G. Denigès.—This paper will be inserted in full.

Composition and Analysis of Yeast.—P. Guichard.—As regards the ultimate analysis of yeast, authorities are not unanimous. Thus, the carbon is made to vary from 34·6 (Liebig) to 52·5 (Wagner), the nitrogen from 7·41 to 15·0, the hydrogen from 6·2 to 7·3, and the oxygen and sulphur, taken together, from 27·1 to 36·4. For the assay of yeast (its fermentative power) the author quotes the processes of Hayduck, Meissl, Mercier, and Billet.

Number of Isomers possible in a Carboniferous Molecule.—M. Delaunay.—A lengthy paper, intelligible doubtless to mathematicians.

Preparation of Phosphorus by means of the Reductive Action of Aluminium upon the Salts of Phosphorus, and Action of Aluminium upon the Alkaline and Alkaline-earthy Sulphates and Chlorides. Oxidation and Ignition of Aluminium by Sodium Peroxide.—Dr. A. Rossel.—At a red heat aluminium decomposes more or less all the calcium phosphates except compact phosphates. Bone-ash, phosphorites, fossil bones in powder, if mixed with aluminium, give off phosphorus at a red heat. In the case of bone-ash the reaction is attended with brisk incandescence. A mixture of ignited superphosphate with silica and aluminium in powder explodes at a dull red heat.

Sodium Borosalicylate.—Paul Adam.—The sodium borosalicylate, now known as an antiseptic, is not a mixture, but a definite compound.

Ethyl Phenols.—A. Behal and E. Choay.—This memoir is not adapted for useful abridgment.

Constitution of the Magentas.—A. Rosenstiehl.—A claim of priority. The author's formula, published in 1880, seems to have been adopted by Prof. A. W. von Hofmann in 1885 and by V. von Richter in 1888.

MEETINGS FOR THE WEEK.

TUESDAY, 15th.—Royal Institution, 3. "Rubies—their Nature, Origin, and Metamorphoses," by Prof. J. W. Judd, F.R.S.
—— Pathological, 8.30. (Anniversary).
WEDNESDAY, 16th.—Meteorological, 8.
—— Microscopical, 8.
THURSDAY, 17th.—Chemical, 8. "The Influence of Moisture on Chemical Change," by H. Brereton Baker, M.A. "Volatile Compounds of Lead Sulphide," by J. B. Hannay. "A Specimen of Early Scottish Iron," by Margaret D. Dougal. "The Mineral Waters of Cheltenham," by Professor Thorpe, F.R.S.
—— Royal Institution, 3. "The Solid and Liquid States of Matter," by Prof. Dewar, F.R.S.
FRIDAY, 18th.—Royal Institution, 9. "The Splash of a Drop and allied Phenomena," by Prof. A. M. Worthington, M.A., F.R.S.
—— Quekett Club, 8.
SATURDAY, 19th.—Royal Institution, 3. (The Tyndall Lectures). "On Colour Vision," by Capt. Abney, F.R.S.

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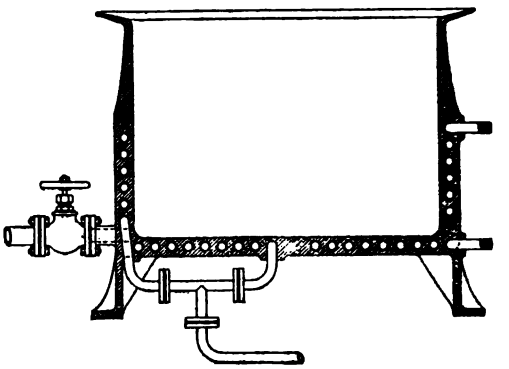

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says:—

P. 316. "An improved vessel for boiling oil, and suitable for many other kindred purposes, has been recently described by T. Frederking (CHEMICAL NEWS, London). A coil of stout piping is arranged in a casting mould, so that the molten metal forming the pan is cast round the coil, much as is done in the case of the water-tuyeres of a blast furnace. Steam at any pressure [or any other heating medium] being passed through the coil, the pan is heated up proportionately without any danger, the pressure bearing solely on the piping and not on the metal pan itself, whilst the well conducting metal walls allow the heat to pass readily. Temperatures up to 350° and 400° C. can be thus obtained."

Messrs. KALLE & Co., Manufacturers of Aniline Colours, Biebrich (Rhine), in their letter of November 22nd, 1893, say:—

"We have tried your Patent Vessel during three months, and have come to the conclusion that it has realised all our expectations. The working pressure of steam has been up to 10 atm. additional pressure; the heating was as efficient and as quickly developed as if the tubes were in the fluid. After having turned off the steam we used the same pipes immediately for cooling by sending water through them, and the vessel, after continued use in this way, proved itself free from cracks or fissures."

Messrs. C. and G. MÜLLER, Rixdorf, near Berlin, S.O., in their letter of December 22nd, 1893, say:—

"Concerning the Patent Vessel which you delivered to us, we beg to inform you that it has been in work four months to our entire satisfaction. The security in working with high pressure is especially satisfactory. With your Patent Vessel we are able to get through much larger quantites of tallow in less time than with our previous plant."

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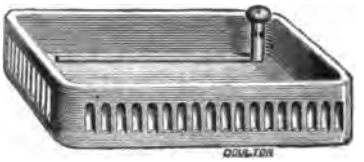

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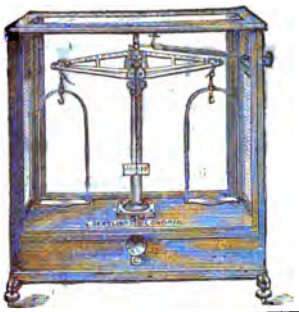

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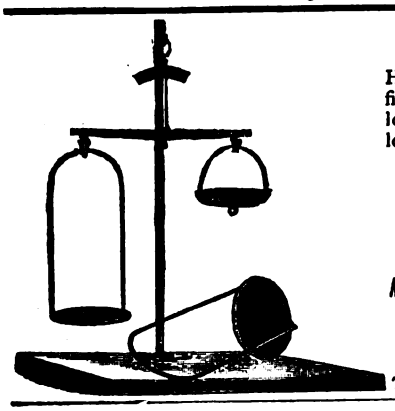

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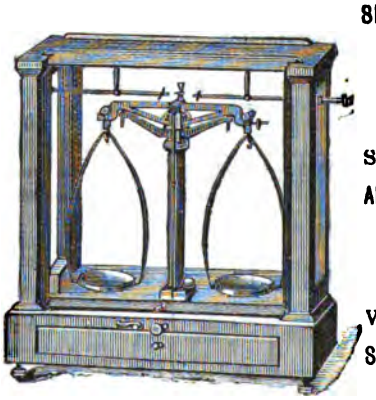

FIG. 3a.

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ON AN ANOMALY ENCOUNTERED IN DETERMINATIONS OF THE DENSITY OF NITROGEN GAS.*

By Lord RAYLEIGH, Sec. R.S.

In a former communication† I have described how nitrogen, prepared by Lupton's method, proved to be lighter by about 1-1000th part than that derived from air in the usual manner. In both cases a red hot tube containing copper is employed, but with this difference. In the latter method the atmospheric oxygen is removed by oxidation of the copper itself, while in Lupton's method it combines with the hydrogen of ammonia, through which the air is caused to pass on its way to the furnace, the copper remaining unaltered. In order to exaggerate the effect, the air was subsequently replaced by oxygen. Under these conditions the whole, instead of only about one-seventh part of the nitrogen is derived from ammonia, and the discrepancy was found to be exalted to about one-half per cent.

Upon the assumption that similar gas should be obtained by both methods, we may explain the discrepancy by supposing either that the atmospheric nitrogen was too heavy on account of imperfect removal of oxygen, or that the ammonia nitrogen was too light on account of contamination with gases lighter than pure nitrogen. Independently of the fact that the action of the copper in the first case was pushed to great lengths, there are two arguments which appeared to exclude the supposition that oxygen was still present in the prepared gas. One of these depends upon the large quantity of oxygen that would be required in view of the small difference between the weights of the two gases. As much as 1-30th part of oxygen would be necessary to raise the density by 1 200th, or about one-sixth of all the oxygen originally present. This seemed to be out of the question. But even if so high a degree of imperfection in the action of the copper could be admitted, the large alteration caused by the substitution of oxygen for air in Lupton's process would remain unexplained. Moreover, as has been described in the former paper, the introduction of hydrogen into the gas made no difference, such hydrogen being removed by the hot oxide of copper subsequently traversed. It is surely impossible that the supposed residual oxygen could have survived such treatment.

Another argument may be founded upon more recent results, presently to be given, from which it appears that almost exactly the same density is found when the oxygen of air is removed by hot iron reduced with hydrogen, instead of by copper, or in the cold by ferrous hydrate.

But the difficulties in the way of accepting the second alternative are hardly less formidable. For the question at once arises, of what gas, lighter than nitrogen, does the contamination consist? In order that the reader may the better judge, it may be well to specify more fully what were the arrangements adopted. The gas, whether air or oxygen, after passing through potash was charged with ammonia as it traversed a small wash-bottle, and thence proceeded to the furnace. The first passage through the furnace was in a tube packed with metallic copper, in the form of fine wire. Then followed a wash-bottle of sulphuric acid by which the greater part of the excess of ammonia would be arrested, and a second passage through the furnace in a tube containing copper oxide. The gas then traversed a long length of pumice charged with sulphuric acid, and a small wash-bottle containing Nessler solution. On the other side of the regulating tap the arrangements were always as formerly described, and included tubes of finely divided potash and of phosphoric anhydride. The rate of passage was usually about half a litre per hour.

Of the possible impurities, lighter than nitrogen, those most demanding consideration are hydrogen, ammonia, and water vapour. The last may be dismissed at once, and the absence of ammonia is almost equally certain. The question of hydrogen appears the most important. But this gas, and hydrocarbons, such as CH_4, could they be present, should be burnt by the copper oxide; and the experiments already referred to, in which hydrogen was purposely introduced into atmospheric nitrogen, seem to prove conclusively that the burning would really take place. Some further experiments of the same kind will presently be given.

The gas from ammonia and oxygen was sometimes odourless, but at other times smelt strongly of nitrous fumes, and, after mixture with moist air, reddened litmus paper. On one occasion the oxidation of the nitrogen went so far that the gas showed colour in the blow-off tube of the Töppler, although the thickness of the layer was only about half an inch. But the presence of nitric oxide is, of course, no explanation of the abnormal lightness. The conditions under which the oxidation takes place proved to be difficult of control, and it was thought desirable to examine nitrogen derived by *reduction* from nitric and nitrous oxides.

The former source was the first experimented upon. The gas was evolved from copper and diluted nitric acid in the usual way, and, after passing through potash, was reduced by *iron*, copper not being sufficiently active, at least without a very high temperature. The iron was prepared from blacksmith's scale. In order to get quit of carbon, it was first treated with a current of oxygen at a red heat, and afterwards reduced by hydrogen, the reduction being repeated after each employment. The greater part of the work of reducing the gas was performed outside the furnace, in a tube heated locally with a Bunsen flame. In the passage through the furnace in a tube containing similar iron the work would be completed, if necessary. Next followed washing with sulphuric acid (as required in the ammonia process), a second passage through the furnace over copper oxide, and further washing with sulphuric acid. In order to obtain an indication of any unreduced nitric oxide, a wash-bottle containing ferrous sulphate was introduced, after which followed the Nessler test and drying tubes, as already described. As thus arranged, the apparatus could be employed without alteration, whether the nitrogen to be collected was derived from air, from ammonia, from nitric oxide, from nitrous oxide, or from ammonium nitrite.

The numbers which follow are the weights of the gas contained by the globe at zero, at the pressure defined by the manometer when the temperature is 15°. They are corrected for the errors in the weights, but not for the shrinkage of the globe when exhausted, and thus correspond to the number 2·31026, as formerly given for nitrogen.

Nitrogen from NO *by Hot Iron.*

November 29, 1893	2·30143
December 2, 1893	2·29890
December 5, 1893	2·29816
December 6, 1893	2·30182
Mean,	2·30008.

Nitrogen from N_2O *by Hot Iron.*†

December 26, 1893	2·29869
December 28, 1893	2·29940
Mean,	2·29904.

* A Paper read before the Royal Society.

† "On the Densities of the Principal Gases," *Roy. Soc. Proc.*, liii., p. 146, 1893.

† The N_2O was prepared from zinc and very dilute nitric acid.

Nitrogen from Ammonium Nitrite passed over Hot Iron.

January 9, 1894	2·29849
January 13, 1894	2·29889

Mean, 2·29869.

With these are to be compared the weights of nitrogen derived from the atmosphere.

Nitrogen from Air by Hot Iron.

December 12, 1893..	2·31017
December 14, 1893..	2·30986 (H)
December 19, 1893..	2·31003 (H)
December 22, 1893..	2·31007

Mean, 2·31003.

Nitrogen from Air by Ferrous Hydrate.

January 27, 1894	2·31024
January 30, 1894	2·31010
February 1, 1894	2·31028

Mean, 2·31020.

In the last case a large volume of air was confined for several hours in a glass reservoir with a mixture of slaked lime and ferrous sulphate. The gas was displaced by deoxygenated water, and further purified by passage through a tube packed with a similar mixture. The hot tubes were not used.

If we bring together the means for atmospheric nitrogen obtained by various methods, the agreement is seen to be good, and may be regarded as inconsistent with the supposition of residual oxygen in quantity sufficient to influence the weights.

Atmospheric Nitrogen.

By hot copper, 1892	2·31026
By hot iron, 1893	2·31003
By ferrous hydrate, 1894	2·31020

Two of the results relating to hot iron, those of December 14 and December 19, were obtained from nitrogen into which hydrogen had been purposely introduced. An electrolytic generator was inserted between the two tubes containing hot iron, as formerly described. The generator worked under its own electromotive force, and the current was measured by a tangent galvanometer. Thus, on December 19, the deflection throughout the time of filling was 3°, representing about $\frac{1}{17}$th ampère. In two hours and a half the hydrogen introduced into the gas would be about 70 c.c., sufficient, if retained, to reduce the weight by about 4 per cent. The fact that there was no sensible reduction proves that the hydrogen was effectively removed by the copper oxide.

The nitrogen, obtained altogether in four ways from chemical compounds, is materially lighter than the above, the difference amounting to about 11 m.grms., or about $\frac{1}{210}$th part of the whole. It is also to be observed that the agreement of individual results is less close in the case of chemical nitrogen than of atmospheric nitrogen.

I have made some experiments to try whether the densities were influenced by exposing the gas to the silent electric discharge. A Siemens tube, as used for generating ozone, was inserted in the path of the gas after desiccation with phosphoric anhydride. The following were the results:—

Nitrogen from Air by Hot Iron, Electrified.

January 1, 1894	2·31163
January 4, 1894	2·30956

Mean, 2·31059.

Nitrogen from N_2O by Hot Iron, Electrified.

January 2, 1894	2·30074
January 5, 1894	2·30054

Mean, 2·30064.

The somewhat anomalous result of January 1 is partly explained by the failure to obtain a subsequent weighing of the globe empty, and there is no indication that any effect was produced by the electrification.

One more observation I will bring forward in conclusion. Nitrogen prepared from oxygen and ammonia, and about one-half per cent lighter than ordinary atmospheric nitrogen, was stored in the globe for eight months. The globe was then connected to the apparatus, and the pressure was re-adjusted in the usual manner to the standard conditions. On re-weighing no change was observed, so that the abnormally light nitrogen did not become dense by keeping.

ACTION OF CHLORINE IN PRESENCE OF H_2SO_4.

By C. H. DARLING, A.R.C.S. Ireland.

In consequence of some experiments made by Professor Hodgkinson on the action of chlorine on some fluorene and acenaphthene derivatives dissolved in concentrated H_2SO_4, it was suggested to me to investigate the action of halogens on several other substances under similar circumstances. I have therefore tried a number of preliminary experiments, the results of which are appended in tabular form.

The acid employed as solvent was ordinary concentrated sulphuric. The substances were either dissolved in this or, where insoluble, covered with it to a depth of 3 to 4 c.m. The chlorine was obtained as usual here from HCl and $K_2Mn_2O_8$, and dried by passing through three washing-bottles with concentrated sulphuric acid.

Action of Cl, Br, and I on Bodies in the Presence of Concentrated H_2SO_4.

Substance taken.	Treated with.	Temperature raised to.	Result.
Mon-nitrobenzene	Cl	About 150° C.	Body unchanged.
Di-nitrobenzene .	Cl	„ 150° C.	„
Aniline	Cl	„ 150° C.	„
Methyl aniline ..	Cl	„ 150° C.	„
Cinnamic acid ..	Cl	„ 80° C.	„
„ „ ..	Br	„ 80° C.	„
Benzoic „ ..	Cl	„ 50° C.	„
„ „ ..	Br	„ 50° C.	„
Phthalic „ ..	Br	„ 70° C.	„
Phenol	Cl	„ 80° C.	„
Zinc	Cl	„ 100° C.	„
Antimony	Cl	„ 150° C.	„
Mercury	Cl	„ cold.	Slightly chlorinated.
„	I	„ 250° C.	No action until H_2SO_4 boiled, when a double sulphate was formed.
Phosphorus, yellow	Cl	Cold.	Rather strongly chlorinated.
„ amorph.	Cl	Cold.	Scarcely acted upon.

Woolwich.

Society of Chemical Industry (Nottingham Section.)—At the next meeting at University College, Nottingham, on Wednesday, May 23rd, at 7.30 p.m., a paper will be read "On Commercial Analysis of Lard," by Messrs. Schweitzer and Lungwitz. Visitors are invited.

THE METHODS OF SUGAR ANALYSIS.*

(Continued from p. 224).

Reducing Sugars (continued).

(c) Allihn's Gravimetric Method for the Determination of Dextrose.—

Reagents:

I. 34·639 grms. of $CuSO_4,5H_2O$, dissolved in water and diluted to 500 c.c.

II. 173 grms. of Rochelle salts, 125 grms. of KOH, dissolved in water and diluted to 500 c.c.

Place 30 c.c. of the copper solution (I.), 30 c.c. of the alkaline tartrate solution (II.), and 60 c.c. of water in a beaker, and heat to boiling. Add 25 c.c. of the solution of the material to be examined, which must be so prepared as not to contain more than 1 per cent of dextrose, and boil for two minutes. Filter immediately without diluting, and obtain the weight of copper by one of the methods given under (*c*). The corresponding weight of dextrose is found by the following Table:—

Allihn's Table for the Determination of Dextrose.†

M.grms. of copper.	M.grms. of dextrose.	M.grms. of copper.	M.grms. of dextrose.
10	6·1	57	29·3
11	6·6	58	29·8
12	7·1	59	30·3
13	7·6	60	30·8
14	8·1	61	31·3
15	8·6	62	31·8
16	9·0	63	32·3
17	9·5	64	32·8
18	10·0	65	33·3
19	10·5	66	33·8
20	11·0	67	34·3
21	11·5	68	34·8
22	12·0	69	35·3
23	12·5	70	35·8
24	13·0	71	36·3
25	13·5	72	36·8
26	14·0	73	37·3
27	14·5	74	37·8
28	15·0	75	38·3
29	15·5	76	38·8
30	16·0	77	39·3
31	16·5	78	39·8
32	17·0	79	40·3
33	17·5	80	40·8
34	18·0	81	41·3
35	18·5	82	41·8
36	18·9	83	42·3
37	19·4	84	42·8
38	19·9	85	43·4
39	20·4	86	43·9
40	20·9	87	44·4
41	21·4	88	44·9
42	21·9	89	45·4
43	22·4	90	45·9
44	22·9	91	46·4
45	23·4	92	46·9
46	23·9	93	47·4
47	24·4	94	47·9
48	24·9	95	48·4
49	25·4	96	48·9
50	25·9	97	49·4
51	26·4	98	49·9
52	26·9	99	50·4
53	27·4	100	50·9
54	27·9	101	51·4
55	28·4	102	51·9
56	28·8	103	52·4
104	52·9	178	91·1
105	53·5	179	91·6
106	54·0	180	92·1
107	54·5	181	92·6
108	55·0	182	93·1
109	55·5	183	93·7
110	56·0	184	94·2
111	56·5	185	94·7
112	57·0	186	95·2
113	57·5	187	95·7
114	58·0	188	96·3
115	58·6	189	96·8
116	59·1	190	97·3
117	59·6	191	97·8
118	60·1	192	98·4
119	60·6	193	98·9
120	61·1	194	99·4
121	61·6	195	100·0
122	62·1	196	100·5
123	62·6	197	101·0
124	63·1	198	101·5
125	63·7	199	102·0
126	64·2	200	102·6
127	64·7	201	103·1
128	65·2	202	103·7
129	65·7	203	104·2
130	66·2	204	104·7
131	66·7	205	105·3
132	67·2	206	105·8
133	67·7	207	106·3
134	68·2	208	106·8
135	68·8	209	107·4
136	69·3	210	107·9
137	69·8	211	108·4
138	70·3	212	109·0
139	70·8	213	109·5
140	71·3	214	110·0
141	71·8	215	110·6
142	72·3	216	111·1
143	72·9	217	111·6
144	73·4	218	112·1
145	73·9	219	112·7
146	74·4	220	113·2
147	74·9	221	113·7
148	75·5	222	114·3
149	76·0	223	114·8
150	76·5	224	115·3
151	77·0	225	115·9
152	77·5	226	116·4
153	78·1	227	116·9
154	78·6	228	117·4
155	79·1	229	118·0
156	79·6	230	118·5
157	80·1	231	119·0
158	80·7	232	119·6
159	81·2	233	120·1
160	81·7	234	120·7
161	82·2	235	121·2
162	82·7	236	121·7
163	83·3	237	122·3
164	83·8	238	122·8
165	84·3	239	123·4
166	84·8	240	123·9
167	85·3	241	124·4
168	85·9	242	125·0
169	86·4	243	125·5
170	86·9	244	126·0
171	87·4	245	126·6
172	87·9	246	127·1
173	88·5	247	127·6
174	89·0	248	128·1
175	89·5	249	128·7
176	90·0	250	129·2
177	90·5	251	129·7

* Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (American) at its Meeting at Chicago, August, 1893.

† *Journ. Prakt. Chem.*, 1880, xxii., 46.

M.grms. of copper.	M.grms. of dextrose.	M.grms. of copper.	M.grms. of dextrose.	M.grms. of copper.	M.grms. of dextrose.	M.grms. of copper.	M.grms. of dextrose.
252	130·3	326	170·9	400	212·9	432	231·6
253	130·8	327	171·4	401	213·5	433	232·2
254	131·4	328	172·0	402	214·1	434	232·8
255	131·9	329	172·5	403	214·6	435	233·4
256	132·4	330	173·1	404	215·2	436	233·9
257	133·0	331	173·7	405	215·8	437	234·5
258	133·5	332	174·2	406	216·4	438	235·1
259	134·1	333	174·8	407	217·0	439	235·7
260	134·6	334	175·3	408	217·5	440	236·3
261	135·1	335	175·9	409	218·1	441	236·9
262	135·7	336	176·5	410	218·7	442	237·5
263	136·2	337	177·0	411	219·3	443	238·1
264	136·8	338	177·6	412	219·9	444	238·7
265	137·3	339	178·1	413	220·4	445	239·3
266	137·8	340	178·7	414	221·0	446	239·8
267	138·4	341	179·3	415	221·6	447	240·4
268	138·9	342	179·8	416	222·2	448	241·0
269	139·5	343	180·4	417	222·8	449	241·6
270	140·0	344	180·9	418	223·3	450	242·2
271	140·6	345	181·5	419	223·9	451	242·8
272	141·1	346	182·1	420	224·5	452	243·4
273	141·7	347	182·6	421	225·1	453	244·0
274	142·2	348	183·2	422	225·7	454	244·6
275	142·8	349	183·7	423	226·3	455	245·2
276	143·3	350	184·3	424	226·9	456	245·7
277	143·9	351	184·9	425	227·5	457	246·3
278	144·4	352	185·4	426	228·0	458	246·9
279	145·0	353	186·0	427	228·6	459	247·5
280	145·5	354	186·6	428	229·2	460	248·1
281	146·1	355	187·2	429	229·8	461	248·7
282	146·6	356	187·7	430	230·4	462	249·3
283	147·2	357	188·3	431	231·0	463	249·9
284	147·7	358	188·9				
285	148·3	359	189·4				
286	148·8	360	190·0				
287	149·4	361	190·6				
288	149·9	362	191·1				
289	150·5	363	191·7				
290	151·0	364	192·3				
291	151·6	365	192·9				
292	152·1	366	193·4				
293	152·7	367	194·0				
294	153·2	368	194·6				
295	153·8	369	195·1				
296	154·3	370	195·7				
297	154·9	371	196·3				
298	155·4	372	196·8				
299	156·0	373	197·4				
300	156·5	374	198·0				
301	157·1	375	198·6				
302	157·6	376	199·1				
303	158·2	377	199·7				
304	158·7	378	200·3				
305	159·3	379	200·8				
306	159·8	380	201·4				
307	160·4	381	202·0				
308	160·9	382	202·5				
309	161·5	383	203·1				
310	162·0	384	203·7				
311	162·6	385	204·3				
312	163·1	386	204·8				
313	163·7	387	205·4				
314	164·2	388	206·0				
315	164·8	389	206·5				
316	165·3	390	207·1				
317	165·9	391	207·7				
318	166·4	392	208·3				
319	167·0	393	208·8				
320	167·5	394	209·4				
321	168·1	395	210·0				
322	168·6	396	210·6				
323	169·2	397	211·2				
324	169·7	398	211·7				
325	170·3	399	212·3				

(*f*) *Modified Method of Formanek for Electrolytic Estimation of Reduced Copper.*—To the solution obtained by the treatment of the precipitated suboxide with nitric acid and hot water add a sufficient quantity of water to reduce the nitric acid content of the solution below 5 per cent, and electrolyse.

Instead of dissolving the suboxide with nitric acid on the filter, the asbestos filter and contents are transferred from the funnel to the beaker used in the precipitation, and the funnel is washed out with a 4 per cent nitric acid solution. This acid solution is added to the contents of the beaker until a bulk of about 200 c.c. is attained.

Two platinum cylinders are then immersed in the liquid and connections are made with a battery, the larger cylinder being the cathode.

(To be continued).

SEPARATIONS OF METALS.*

By P. JANNASCH and P. ETZ.

I. *On New Quantitative Separations of Metals of the Sulphuretted Hydrogen Group in a Current of Bromine Vapour or of Chlorine.*

The separation of these metals in a current of bromine vapour instead of in chlorine is not only more convenient, but has the advantage that the degrees of volatilisation of the metallic bromides differ more widely among each other than those of the corresponding chlorides.

In the separation of bismuth and cadmium the authors use cadmium sulphate and metallic bismuth. These substances are dissolved in nitric acid, the solution is evaporated on the water-bath, and the residue is taken up with so much hydrochloric acid that on the addition of about 100 c.c. of water no basic bismuth chloride is deposited. The solution is heated to the temperature of ebullition, the metals are precipitated as sulphides by

* *Journal f. Prakt. Chemie* and *Berichte.*

means of a current of sulphuretted hydrogen, the precipitate is collected on a filter which has been dried at 100°, and weighed, washed with warm sulphuretted hydrogen water, and then thoroughly dried in the air-bath for a determination of its weight.

The dried mixture of sulphides is placed in a porcelain boat in a dried tube of potash-glass, and a brisk current of air which has traversed a glass cylinder containing bromine is passed over it. Bromine acts upon the sulphide even in the cold, but it is soon necessary to support, expedite, and complete the reaction by a gentle heat obtained from a gas flame 1½ inches in height kept in a waving motion.

In about thirty minutes all the bismuth is driven into the receivers containing very weak hydrochloric acid, whilst all the cadmium remains in the boat in the state of bromide. The cadmium bromide was dissolved in a little dilute hydrochloric acid, and precipitated at the heat of ebullition by sodium carbonate.

The solution of bismuth obtained out of the receivers is evaporated, and this operation is repeated two or three times after additions of nitric acid in order to expel the hydrochloric acid, which might interfere in the subsequent precipitation. Finally, the bismuth is separated by boiling with a mixture of ordinary ammonium carbonate and a little ammonia.

In this novel method of separation, particular care must be taken that the mixture of sulphides is perfectly dry when it is exposed to the current of bromine, as otherwise there might be formed a small quantity of a non-volatile basic bismuth salt. A white solid substance, which in some circumstances remains in the combustion-tube, was found to be bismuth oxybromide, readily soluble in cold dilute acid.

It must further be remembered that towards the conclusion of the process the porcelain boat must not be heated so strongly that small shimmering leaflets of cadmium bromide begin to be mixed with the gaseous current. In the precipitation by sulphuretted hydrogen very minute quantities (0·0010 to 0·0015 grm.) of cadmium oxide remain in solution, which may be prevented by a corresponding partial saturation of the free hydrochloric acid with sodium carbonate in the course of precipitation.

The separation of bismuth from lead may be effected in a similar manner. The separation of these metals in a current of chlorine has been lately effected in a form capable of absolutely accurate execution by W. Remmler (*Berichte*, xxiv., 3554). He heats the sulphides of both metals in a current of chlorine for an hour, first in Victor Meyer's xylol boiler, and then for another hour in a sulphur-bath, *i.e.*, in the vapour of boiling sulphur. All the bismuth chloride is volatilised, whilst the lead chloride is left quantitatively. As here the bismuth chloride formed is driven into the air, the bismuth is not determined directly, but as loss. Hence this method ranks as an indirect quantitative method, though by a slight modification of the apparatus it will be easy to render the Meyer-Remmler process direct.

For separation in a current of bromine vapour, Jannasch and Etz dissolve metallic bismuth and pure lead nitrate in dilute nitric acid. The metallic salts are evaporated to dryness, taken up in water and the necessary quantity of hydrochloric acid precipitated with sulphuretted hydrogen from a hot and rather dilute solution. The precipitated sulphides are dried at 100°, and heated in a current of air and bromine in a previously weighed boat. Bismuth bromide distils over completely, and lead bromide remains fused in the boat, in a state sufficiently free for the quantitative determination of the lead. In the receivers for intercepting the bismuth bromide there is put very dilute nitric acid.

The following precautions are absolutely necessary for success:—

In the first place, the sulphides obtained with sulphuretted hydrogen must not be allowed to stand a long time either in the liquid or in the funnels, but must be worked up as rapidly as possible. The authors find that a prolonged exposure of the mixed sulphides to air is decidedly injurious, and may even lead to perfectly worthless results. Such precipitates, on subsequent treatment in the current of bromine vapour, yield not pure bromides, but at the same time basic compounds, a circumstance which interferes more or less with the complete volatilisation of the bismuth.

(To be continued.)

DETERMINATION OF GLYCERIN IN WINE.

By HARMAR DENNY PAXTON, M.S.

The methods for the determination of glycerin are for the most part inaccurate and unsatisfactory, owing to the extreme difficulty of obtaining it in a pure condition, and on account of the loss by volatilisation when its solution is heated in open vessels.

The great importance of the determination of glycerin in wine and beer, &c., makes it necessary to employ a more convenient and accurate method than those now in use.

The method of the Berlin Commission, even as modified by Barth (compare "Annual Report of the Dairy Commissioner of New Jersey, 1892, p. 81) and that of Lecco (*Chem. Zeit.*, 1892, No. 30, 5, 504), both involve the following:—Evaporation of the wine and extraction of the glycerin with alcohol in open vessels, evaporation of the alcoholic extract, taking up the residue with ether and alcohol, and final evaporation of the latter in a weighing tube.

To show that in all of the foregoing operations there is some glycerin either lost or unextracted, the following experiment was made:—

100 c.c. of claret, to which a definite amount of pure glycerin was added, was treated according to the Commission method. On weighing the total extracted glycerin there was found to be a loss which, expressed in per cent, was equal to 3·51 per cent.

Like experiments on the Lecco method gave a much larger loss = 11·00 per cent.

To make the extraction more thorough and complete, and to obviate the necessity of performing the operation in open vessels, a method was tried as follows:—

Ten c.c. of claret was treated with a sufficient quantity of slaked lime, transferred, drop by drop, to a piece of stretched out filter-paper, and allowed to dry at the ordinary temperature. This was folded, placed in a Soxhlet's apparatus, and extracted with absolute alcohol. The alcoholic extract was evaporated in a flask with a long neck, taken up with ether-alcohol, allowed to stand, transferred (filtered if necessary) to weighing-tube, evaporated, dried, and weighed.

The use of the Soxhlet's apparatus has the advantage of convenience and ease, affording a more thorough and complete extraction without so much loss of glycerin by volatilisation.

Experiments were made upon each of the foregoing methods as follows:—

Commission Method.

	Grms.	Grm. per 10 c.c.
Expt. I. 100 c.c. claret gave glycerin	= 1·0138	or 0·1014
„ II. „ „ „	= 0·7988	or 0·0799

Lecco Method.

Expt. III. 10 c.c. claret gave glycerin	= 0·0933 grm.
„ IV. „ „ „	= 0·0898 „

Using Soxhlet's Apparatus.

Expt. V. 10 c.c. claret gave glycerin	= 0·1025 grm.
„ VI. „ „ „	= 0·1273 „

The same brand of claret was used in every case.

By a comparison of these results it will be seen that those by the Soxhlet's apparatus are higher than either of the others, and that the duplicates correspond as well as those by the Commission method.

The resulting glycerin appeared to be as pure as that obtained by the other methods.

John C. Green School of Science,
Princetown, New Jersey, April 11, 1894.

THE DETERMINATION OF THE STRENGTH OF SULPHURIC ACID.

By H. DROOP RICHMOND.

THREE years ago Pickering, and Lunge and Isler, published nearly simultaneously investigations of the density of sulphuric acid of different strengths. These determinations differed materially, and consequently the table which I drew up from Pickering's results was not in accord with that published by Lunge and Isler. A discussion took place in the CHEMICAL NEWS in which both Pickering and Lunge affirmed the correctness of their own results.

Having had occasion to make up a series of samples of sulphuric acid of different concentration, I determined the density of these, and calculated the percentage of real acid by each table. I started with an acid which, by weighing as ammonium sulphate, showed 96·69 and 96·60 per cent of H_2SO_4, and had a density of 1·8429, which by both tables agrees to 0·0001 with the mean of the two determinations. Quantities of about 250 grms. were weighed out in stoppered bottles, and weighed quantities of water added; the mixing was performed with the stopper in the bottle, so as to prevent loss. The error in making up the solutions did not exceed 0·04 per cent; the densities at 15° C. were (water at 15° = 1, reduced to vacuum standard):—

Strength calculated from dilution.	Density.	Original acid. Richmond.	Original acid. Lunge and Isler.
94·92	1·83995	96·66	96·40
93·48	1·8358	96·66	96·22
92·88	1·8334	96·58	96·14
92·03	1·8303	96·66	96·40
91·76	1·8289	96·60	96·31

Having made a considerable number of density determinations with the same apparatus (a 10 c.c. Sprengel tube), I have found that my density determinations are accurate to 0·0002; my thermometer had been standardised at Kew, and was read to 0·1 degree. The deviations from the densities given in my table for the various strengths of acid is in three cases less than 0·0001; in one case it reaches that figure, and in two cases it is 0·0002; in other words, the difference is within the known possible errors of making up the solutions and taking the density. The differences, using Lunge and Isler's table, amount to five or six times the possible error.

A Nordhausen acid fairly, but not quite, pure showed by the ammonium sulphate method 105·72 per cent H_2SO_4 (or anhydride equivalent to this). This was mixed with the former acid to produce an acid of 99·98 per cent (calc.). The density was 1·8393, an impossible density when using Lunge and Isler's tables, and 0·0008 too high using mine. This acid developed 0·04 per cent sulphurous anhydride. By mixing 38·793 grms. with 2·097 grms. water I obtained an acid of a density 1·8398; this corresponds to 99·99 per cent for the original acid. When it is remembered that any impurities would lower the apparent strength of the undiluted acid, and raise that of the diluted acid, that the acid was not quite pure, and that owing to the development of SO_2 the acid was less than 99·98 per cent; these results also point to my table, deduced from Pickering's results, being the accurate one, and to that of Lunge and Isler being quite wrong. Indeed, after the condemnation supplied by Lunge himself, when he says that titration estimations are already *very* good when they agree to 0·1 per cent, I can hardly understand Lunge and Isler claiming that their table is exact. When it is remembered, also, that Pickering's densities were determined to the sixth place of decimals, and his percentages were known relatively to the fourth and absolutely to the second place, it is difficult to see how errors in the third place of decimals in the densities, and the first place in the percentages, can have been made by him, as would be the case were Lunge and Isler's contention correct.

THE EIGHTH INTERNATIONAL CONGRESS OF HYGIENE AND DEMOGRAPHY.

THIS Congress, to be held at Budapest from the 1st to the 9th of September, 1894, is under the patronage of the Emperor of Austria and the presidency of Count Stephen Karolyi.

The last meeting was held in London in 1891, and in accordance with the arrangements then made, the Executive Committee now invite the members to this meeting in Austria-Hungary.

The Hygienic Section is divided into XIX. sub-sections, comprising hygiene in relation to all manner of subjects, such as infectious and epidemic diseases, food, towns, military service, railroads, ships, sport, &c., &c.; while the Demographic Section deals with that subject in VII. sub-sections, including historical, general, anthropometrical, the conditions of agricultural and industrial labourers from the demographic point of view, &c. Up to March 31st there were already 535 papers and lectures on the list, so the success of the scientific part of the Congress seems to be already assured.

The fee for membership is ten florins for gentlemen and five for ladies; which will carry with it exceptional advantages with regard to railway travelling, hotels, and lodgings. There will be a number of receptions, fêtes, and excursions, and thorough arrangements are being made for carrying everything out with the utmost order and comfort.

Further details can be obtained from the Secretary-General, St. Rochus Hospital, Budapest, to whom subscriptions may be sent.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 19th, 1894.

Dr. H. E. ARMSTRONG, President, in the Chair.

(Concluded from p. 227).

*136. "*Natural Oxycelluloses. I. Celluloses of the Gramineæ.*" By C. SMITH.

The experiments, of which this communication is a preliminary account, are undertaken in extension of the results recently obtained by Messrs. Cross, Bevan, and Beadle (*Ber.*, 1893).

The "celluloses" of esparto and the cereal straws, as isolated by the well-known processes of the paper-maker, were further purified, and (1)) their ultimate composition, (2) the amount of furfural obtained an boiling with aqueous hydrochloric acid (1·06 rel. dens.) with the following results.

	(1).		(2).
	C.	H.	Furfural, p.c.
Straw "Cellulose" ..	42·4	5·8	12·5
Esparto "Cellulose" ..	41·4	5·6	12·2

These "celluloses," therefore, are oxycelluloses, and, since they do not give the reactions characteristic of the pentoses, they are of the type of those obtained by Cross and Bevan by regulated oxidation of the normal celluloses (*loc. cit.*).

Such oxycelluloses being widely distributed in nature, it becomes important to study their physiology. A course of systematic observations has therefore been undertaken on the germination and growth of the barley plant in relation to the composition and constitution of its permanent tissue ("cellulose").

It has already been observed that, by germination in the dark and growth of the sprouts (etiolated) until the endosperm is nearly exhausted, there is a considerable increase in the furfural-yielding constituents (60—80 per cent), the early material of the tissue giving 5 per cent furfural, and at the same time no pentose reaction, which proves it to be an oxycellulose. The results are still more marked in the case of the tissues of plants grown in the light.

DISCUSSION.

Mr. WARINGTON hoped that the authors would continue this investigation, as the subject was of much importance in relation to the digestibility of animal food. They had already established the important fact that the production of furfural can no longer be utilised for the estimation of the pentoses, since the oxycelluloses also furnish this compound.

*137. "*Preliminary Note on the Volatilisation of Salts during Evaporation.*" By G. H. BAILEY, D.Sc., Ph.D.

From experiments, carried out for the most part with the chlorides of the alkali metals, it was found that an appreciable amount of the salt was lost during evaporation of the aqueous solutions, although every precaution was used to prevent this occurring mechanically.

The amount of loss was found to be greater with the haloid compound of elements of higher atomic weight, and also greater the more concentrated the solution.

With lithium chloride of about one-fifth normal strength it amounted to 0·35 m.grm. per litre of water evaporated, and with calcium chloride of the same strength, 2·4 m.grms., whilst with lithium chloride containing about 38 grms. to the litre the loss was 2·45 m.grms., and with cæsium chloride containing 286 grms. to the litre it was 18·86 m.grms.

From the results obtained, it seems likely that when accurate determinations have been made on a more extended scale they may be the means of throwing light on the nature of solution and upon the vapour tension and vapour density of salts at comparatively low temperatures.

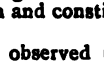
The observations also reveal a source of error which, in the case of some estimations, will involve the making of a large correction, and which must, at all events, receive consideration in all investigations where a high degree of accuracy is of essential importance.

138. "*Constitution of Glycocine and its Derivatives.*" By JOJI SAKURAI, Professor of Chemistry, Imperial University, Japan.

Glycocine is usually represented as amido-acetic acid—

$$NH_2{\cdot}CH_2{\cdot}CO_2H,$$

but, as was first suggested by Erlenmeyer and Sigel (*Ann.* clxxvi., 349), it ought to be regarded as an internal ammonium salt of the constitution—



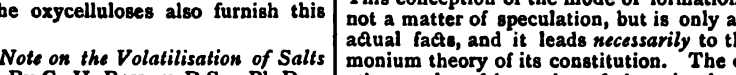
the analogy of glycocine with betaïne, and its behaviour towards mustard oils (Marckwald and others, *Ber.* xxiv., 3279) supporting the latter view of its constitution. Other properties of glycocine are also in best accordance with the latter formula, and there is not a single reaction which needs to be expressed by the ordinarily employed open formula.

That, in spite of the evident claim of the internal ammonium theory to be exclusively adopted, the open formula is almost universally employed is due, partly, at any rate, to the erroneous manner in which the formation of glycocine has been hitherto represented. The change which occurs when ammonia acts upon chloracetic acid is not to be represented merely by the diagram—

$$NH_2|H + Cl|CH_2{\cdot}CO_2H,$$

We must admit that, in this case, ammonia not only goes to neutralise chloracetic acid, but also to form an ammonium chloride, the latter part of this change being analogous to that which occurs when ammonia acts on alkyl halides:—

the ammonium compound thus formed then decomposing, by the action of heat, into glycocine and ammonium chloride:—



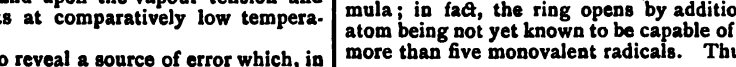
This conception of the mode of formation of glycocine is not a matter of speculation, but is only an expression of actual facts, and it leads *necessarily* to the internal ammonium theory of its constitution. The consideration of other modes of formation of glycocine leads to the same conclusion.

Again, the modes of formation of sarkosine and betaïn can only be satisfactorily expressed in a manner similar to that above described in the case of glycocine.

Hippuric acid, like glycocine itself, must also be represented as a closed chain—

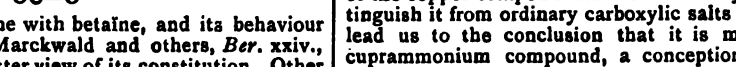
its acid character, feeble as it is, is easily understood from the circumstance that the nitrogen is combined with an acid group, namely, COC_6H_5. That hippuric acid and other amido-acids do not contain the group CO_2H, is supported by the fact that all attempts hitherto made to obtain acid chlorides from them have been attended with failure.

The formation of *addition compounds* of glycocine presents no difficulties to the acceptance of the closed formula; in fact, the ring opens by addition, the nitrogen atom being not yet known to be capable of combining with more than five monovalent radicals. Thus—



It is to be observed that in order to explain the formation of the potassium salt by the ordinary formula of glycocine we must suppose that a double decomposition first occurs with formation of potassium amido-acetate and nitric acid, and that the latter then unites to the amidogen group.

Passing now to the *metallic derivatives* of glycocine, their formation likewise finds a most satisfactory explanation in the closed formula. Thus, the deep blue colour of the copper compound and its solubility in alkalis distinguish it from ordinary carboxylic salts of copper, and lead us to the conclusion that it is most probably a cuprammonium compound, a conception which can be easily expressed in the following manner:—



If, however, we regarded the copper compound as an amidated derivative, and gave it the constitution—

$$Cu(NH\cdot CH_2\cdot CO_2H)_2,$$

we should have to make the baseless assumption that the hydrogen of the carboxyl group remains unreplaced by copper, even when digested with an excess of cupric oxide. If, on the other hand, we regarded it as—

$$(NH_2\cdot CH_2\cdot CO_2)_2Cu,$$

taking glycocine as a carboxylic compound (an acid), because it dissolves oxide of copper and some other metallic oxides, we might argue that ammonium chloride or even ammonia itself is also an acid!

Silver glycocine must likewise be regarded as having the constitution—

$$\begin{array}{l} H_2C—NH_2Hg \\ \quad | \quad | \\ OC—O \end{array} ;$$

this formula can alone account for the formation of amido-acetic ether, on the one hand, by the action of ethyl iodide—

$$\begin{array}{l} H_2C—NH_2Ag \\ \quad | \quad | \\ OC—O \end{array} + C_2H_5I = \begin{array}{l} HC—NH_2AgI \\ \quad | \\ OC—OC_2H_5 \end{array} =$$

$$= \begin{array}{l} H_2C—NH_2 \\ \quad | \\ OC—OC_2H_5 \end{array} + AgI,$$

and the formation of hippuric acid, on the other, by the action of benzoyl chloride—

$$\begin{array}{l} H_2C—NH_2Ag \\ \quad | \quad | \\ OC—O \end{array} + C_6H_5CO\cdot Cl =$$

$$= \begin{array}{l} H_2C—NH_2\cdot COC_6H_5 \\ \quad | \quad | \\ OC—O \end{array} + AgCl.$$

It must be observed that in the latter change an opening of the ring, as in the case of the action of ethyl iodide on silver glycocine, could not occur, because both the radicles Cl and COC_6H_5 are negative.

If, on the other hand, silver glycocine were regarded either as $NHAg\cdot CH_2\cdot CO_2H$ or $NH_2\cdot CH_2\cdot CO_2Ag$, we could not satisfactorily explain the formation of amido-acetic ether and of hippuric acid respectively.

The examination of the properties of di- and tri-glycolamidic acids which are always represented as $NH(CH_2\cdot CO_2H)_2$ and $N(CH_2\cdot CO_2H)_3$ respectively, goes to further support the correctness of the closed formula for glycocine. These compounds behave only as mono- and di-basic acids towards alkalis and alkaline earths; it is only those of their salts, which contain silver, copper, and a few other metals, more or less characterised by the ease with which they form ammoniated derivatives, that may be regarded as di- and tri-basic. These facts are inexplicable by their accepted constitution, but receive an ample explanation from the following formulæ:—

Diglycolamidic acid.

$$\begin{array}{l} H_2C—NH_2\cdot CH_2\cdot CO_2H \\ \quad | \quad | \\ OC—O \end{array}$$

Triglycolamidic acid.

$$\begin{array}{l} H_2C—NH(CH_2\cdot CO_2H)_2 \\ \quad | \quad | \\ OC—O \end{array}$$

All the so-called amido-acids must be regarded as constituted like glycocine. Thus asparagine and aspartic acids should be respectively represented by the formulæ—

$$\begin{array}{l} CO—O \\ \quad | \quad | \\ C_2H_3\cdot NH_3 \\ \quad | \\ CO\cdot NH_2 \end{array} \quad \text{and} \quad \begin{array}{l} CO—O \\ \quad | \quad | \\ C_2H_3\cdot NH_3, \\ \quad | \\ CO\cdot OH \end{array}$$

a view which is supported by the properties of these compounds. According to this conception, there should exist not only two chemically isomeric asparagins, as is predicted by the current theory, but also two aspartic acids, represented by—

$$\begin{array}{l} CO—O \\ \quad | \quad | \\ CH—NH_3 \\ \quad | \\ CH_2 \\ \quad | \\ CO—OH \end{array} \quad \text{and} \quad \begin{array}{l} CO—OH \\ \quad | \\ CH—NH_3 \\ \quad | \quad | \\ CH_2 \\ \quad | \quad | \\ CO—O \end{array} .$$

At present only one aspartic acid is known, but there are reasons to believe that another will be discovered.

Finally, the term "amido-acids" should be dropped from chemical nomenclature, in accordance with the internal ammonium theory of the constitution of these compounds, and replaced by the words *glycocines* and *taurines*, to be applied respectively to the so-called amido-carboxylic acids and amido-sulphonic acids. Thus, alanine, asparagine, and aspartic acid should be called *propionic*, *succinamic*, and *succinic glycols* respectively, whilst γ-amido-propyl sulphonic acid (Gabriel and Lauer, *Ber.*, xxii., 2988) should be changed to *trimethylene-taurine* and represented by the formula—

$$CH_2\begin{array}{l}<CH_2\cdot NH_3 \\ <CH_2\cdot SO_2\end{array}>O.$$

139. "*Note on the Constitution of Glycocine.*" By James Walker, D.Sc.

In connection with the question as to the constitution of glycocine, which is raised by Professor Sakurai in the foregoing paper, Professor Dunstan suggested that I should bring together any physical facts which might bear on the subject.

Physical methods throw at present little light on the constitution of glycocine. The only question which they decide with certainty is that the molecule of glycocine is not a double molecule of the formula—

$$\begin{array}{l} NH_3\cdot CH_2\cdot CO\cdot O \\ \quad | \quad | \\ O\cdot CO\cdot CH_2\cdot N \end{array}$$

as some have supposed, since the depression of the freezing-point in its aqueous solutions shows that the molecular weight corresponds with the simple, and not with the double, formula. To the objection which might be raised, that this low molecular weight could be due to an electrolytic dissociation of the double molecule, there is the sufficient answer that an aqueous solution of glycocine is an extremely feeble conductor of electricity. I have found that a decinormal solution of the substance does not conduct very many times better than ordinary distilled London water. Whether the slight conductivity is due to the presence of impurities, or to actual electrolytic dissociation of the glycocine, must remain for the present undecided. Even if glycocine were proved to be ionised in aqueous solution, it is not certain what the ions would be, for we do not knew whether under these conditions glycocine acts as an acid or a base. I have shown (*Zeit. Physikal. Chem.*, iv., 331) that glycocine in an equivalent solution of hydrochloric acid acts as a base of nearly the same strength as thiazole; but undoubtedly in an equivalent solution of an alkali it would act in a corresponding manner as an acid. A comparison of the amount of hydrolysis in the two sets of salts may serve to settle whether glycocine in aqueous solution is acid, basic, or strictly neutral, and it is my intention to perform the necessary experiments.

In as far as glycocine behaves as a base, it must, according to Arrhenius's theory, supply hydroxyl ions, which can only come from the compound—

$$NH_3OH\cdot CH_2\cdot COOH,$$

a hydrated form of glycocine, which in its turn might either be derived from $NH_2\cdot CH_2\cdot COOH$, or—

$$\begin{array}{l} CH_2—CO \\ \quad | \quad | \\ NH_3—O \end{array} .$$

It is possible that the hydrated form may exist to a great

extent in solution, while the solid form is anhydrous, for this is undoubtedly the case with betaïne.

While physical methods, then, are mostly silent with regard to the constitution of glycocine itself, they yield decisive evidence that many glycocine derivatives must be represented by an open, and not by a closed, chain. Acetic acid has a dissociation constant K = 0·0018, very many times greater than any that could be attributed to glycocine, which ranks in point of conductivity with the phenols. Phenyl glycocine, $NHPh{\cdot}CH_2{\cdot}COOH$, on the other hand, has a constant K=0·0041, so that the introduction of a phenyl group in the place of one of the hydrogen atoms of the amidogen, has raised the conductivity far above that of acetic acid. Consequently, if acetic acid contains a carboxyl group, phenylglycocine must, *à fortiori*, contain one. The same is evident in still greater degree in the case of hippuric acid, K =, 0·0222, and aceturic acid, K=0·0230. The amido benzoic acids have dissociation constants less than that of acetic acid, but still incomparably greater than that of glycocine, so that they must be regarded as possessing a carboxyl group.

If we are to trust to analogy, therefore, the evidence afforded by electrical conductivity goes to show that glycocine has not the ring constitution, but the ordinarily accepted constitution represented by the formula—

$$NH_2{\cdot}CH_2.COOH.$$

140. "*On the Oxidation of the Alkali Metals.*" By WILMOT HOLT and W. EDGAR SIMS, B.Sc.

The authors have examined the oxides of the alkali metals with a view to ascertain how far stability and composition of the oxides is dependent on the atomic weight of the element from which it is derived, the observations already recorded being so conflicting, and, in many cases, so incomplete, that it was found quite impossible to make any generalisations from them, The general results of their examination are as follows:—

1. Potassium and sodium (and probably lithium) are not attacked by perfectly dry oxygen, and may be distilled in it, without undergoing oxidation.

2. Lithium, when oxidised in oxygen gives rise to the monoxide Li_2O, sodium (a member of the same group, though in the odd series) under certain conditions forms the monoxide Na_2O, whilst in the case of potassium it has been impossible to obtain the monoxide K_2O.

3. The ultimate products of oxidation are: with lithium the monoxide and slight traces of a peroxide; with sodium, the dioxide Na_2O_2; and with potassium, the tetroxide K_2O_4, which must be regarded as the most definite and stable oxides of these metals.

4. The monoxide of potassium, K_2O, is not formed by the oxidation of potassium in any of the oxides of nitrogen as stated by previous observers, and there is no evidence either of the existence of this or of any lower oxide in the pure condition.

5. The only other oxides of which the authors have been able to find any evidence, in addition to those mentioned under Section 3, are Na_2O, K_2O_2, and K_2O_3, these only being obtained under certain conditions owing to their instability.

6. Both potassium and sodium, when oxidised in nitric oxide or the red oxides of nitrogen, form varying mixtures of nitrite and nitrate according to the conditions of the experiment.

Later experiments will probably show that the metals rubidium and cæsium, both of which have higher atomic weight than potassium, will combine with oxygen in still larger proportions.

141. "*The Action of Iodine and of Methyl Iodide on Aconitine.*" By WYNDHAM R. DUNSTAN, F.R.S., and H. A. D. JOWETT, B.Sc.

In 1885 Jürgens described a crystalline dark red *hydriodide of iodaconitine* ($C_{33}H_{46}INO_{12}.HI$), which he had obtained by mixing ethereal solutions of iodine and aconitine, and crystallising the product from chloroform and ether. The percentage of iodine found in the salt agreed closely with the formula given above. By acting on the salt with dilute ammonia he obtained a brown amorphous substance, which he supposed to be iodaconitine. The authors find that when iodine acts on aconitine, dissolved in various liquids, the product is a variable mixture of *aconitine hydriodide*, *aconitine periodide*, and an amorphous neutral substance, which appears to be *iodo-aconitine*, but since it cannot be crystallised it is difficult to characterise. The principal changes may be represented by the equations—

$$1.\ 2C_{33}H_{45}NO_{12}+I_2=C_{33}H_{45}NO_{12},HI+C_{33}H_{44}INO_{12},$$

$$2.\ C_{33}H_{45}NO_{12}HI+xI_2=C_{33}H_{45}NO_{12}HI,xI_2.$$

The crystals obtained by Jürgens consist of an unstable aconitin periodide, which cannot be crystallised without losing iodine. The dark brown crystals originally obtained gradually become lighter on re-crystallisation, and finally are resolved into the colourless aconitine hydriodide. Analysis shows a gradually diminishing percentage of iodine as the re-crystallisation is repeated until pure aconitine hydriodide is obtained. This salt was identified by its melting-point (226°), and also by its furnishing pure aconitine (m. p. 188—189°), when decomposed with dilute ammonia.

The same unstable periodide may be obtained by adding iodine to an aqueous solution of aconitine hydriodide. The brown precipitate is crystallised from its solution in alcohol.

In attempting to isolate iodaconitine, the mixture prepared by adding an ethereal solution of iodine to an ethereal solution of aconitine was dissolved in chloroform, and the solution was shaken with dilute ammonia. By this means a substance was obtained from this solution which contained much aconitine, and also a smaller amount of an amorphous compound, which was separated from aconitine by precipitating a solution in chloroform with ether. All attempts to crystallise this substance have failed. It is a greyish powder, which melts indefinitely near 208°, and is nearly insoluble in cold water, but readily dissolves in alcohol and chloroform. On analysis it furnished the percentage of iodine required by the formula $C_{33}H_{44}INO_{12}$. It does not possess basic properties.

In a previous communication (*Trans.*, li., 403) it has been shown that when aconitine is heated in a closed tube with methyl iodide it dissolves, and that on cooling the solution, crystals separate which contain the percentage of iodine required by aconitine methiodide. This substance has now been further investigated, and it has been found that the action of methyl iodide on aconitine is exceptional.

After re-crystallisation from a mixture of ether and chloroform, the crystals melted at 226°, and agreed in all other respects with *aconitine hydriodide*. The action of methyl iodide on aconitine would seem to be represented by the equation—

$$2C_{33}H_{45}NO_{12}+CH_3I=C_{33}H_{45}NO_{12}HI+ +C_{33}H_{44}(CH_3)NO_{12},$$

but although distinct evidence of this simultaneous production of a methyl aconitine was obtained, all the methods employed to isolate it in a pure state have been unsuccessful. An impure base was obtained which furnished a hydrobromide melting near 218°, but during the precipitation of this salt and the re-generation of the alkaloid from it, decomposition apparently occurred, since aconitine was finally obtained. It would thus appear that if methyl aconitine is formed in this reaction, it is so unstable that it cannot be isolated. Other methods have been tried for its production, but these also have failed to furnish the compound.

Research Fund.

A meeting of the Research Fund Committee will be held in June. Fellows who desire grants are requested

to send their applications to the Secretaries at Burlington House, not later than Tuesday, June 5th.

PHYSICAL SOCIETY.

Ordinary Meeting, May 11th, 1894.

WALTER BAILEY, M.A., Vice-President, in the chair.

A MATHEMATICAL communication on "*Electromagnetic Induction in Plane, Cylindrical, and Spherical Current-Sheets, and its Representation by Moving Trails of Images*," by G. H. BRYAN, M.A., (Part I. General Equations), was read by Dr. C. V. BURTON, who also explained some of the parts in greater detail. After mentioning that the magnetic field due to induced currents in thin conducting sheets placed near moving magnetic poles could be represented by moving trails of images of those poles, the author goes on to say that in the paper the surface conditions which hold at the surfaces of the sheets are deduced directly from the fundamental laws of electromagnetic induction. I. "The total current across any enclosed portion of a surface which always contains the same particles is equal to $1/4\pi$ of the time-integral of the magnetic force round the curve bounding the surface," and II. "The rate of decrease of the surface integral of magnetic induction across any enclosed surface which always contains the same particles is equal to the line-integral of electromotive force round the curve bounding the surface." By working with the scalar magnetic potential instead of vector potential the investigation is simplified. In addition to the above laws the author makes the usual assumptions that displacement currents in the dielectric are so small as to be negligible, and that the induced currents are distributed uniformly through the thickness of the sheet. On these suppositions the surface conditions satisfied by the potentials at the two sides of plane, cylindrical, or spherical sheets are determined, and, with an additional limitation as to the thickness of the sheet fulfilling certain conditions, extended to current sheets of other forms. In the latter part of the paper a synthetic determination of the images in a plane sheet is given and expressed in the form of a definite integral.

In reading the paper to the meeting Dr. Burton pointed out several misprints in the proof.

Prof. MINCHIN showed that equation (1) of the paper ($\Omega_2 - \Omega_1 = 4\pi\phi +$ constant, where Ω_2 and Ω_1 are the magnetic potentials at the two sides of the sheet, and ϕ the current function), could be deduced by purely mathematical reasoning, instead of being based on the laws of electromagnetic induction. Moreover it was true for any function whatever, and did not depend on ϕ being the current function. Equation (2)—

$$\left(\frac{d\Omega_2}{dz} = \frac{d\Omega_1}{dz}\right)$$

followed immediately from the fact that the magnetic force was continuous. The latter part of the paper might be simplified by integrating the linear partial differential equation (15)—

$$\left(\frac{d^2\Omega_1}{dz\,dt} - R\frac{d^2\Omega_1}{dz^2} = -\frac{d_2\Omega_0}{dz\,dt}\right)$$

in the ordinary way, for the form was one for which the auxiliary equations are well known.

Dr. BURTON, in reply, said he thought Mr. Bryan's reason for developing the equations from the laws of electromagnetic induction was to give his work a physical rather than a mathematical basis.

A paper "*on Dielectrics*" was read by Mr. ROLLO APPLEYARD.

In testing the insulation resistance of celluloid by having a sheet pressed between two metal plates, the author noticed that the resistance, which was very high, *decreased* as the time the testing battery was left on increased. The "electrification" (using the word to indicate the rate of diminution of galvanometer deflection) was therefore *negative*. The resistance also diminished greatly with increase of battery power, and a considerable amount of hysteresis was observed, the resistance at any given voltage, after a minute's electrification, depending on the previous history of the specimen. On making contact with the surfaces of the celluloid by mercury instead of by solid metal, the abnormal results disappeared, little or no resistance hysteresis or "electrification" being present, and only a small diminution of resistance with increase of voltage. For a 6 mil sheet the resistance between opposite faces 5½ inches diameter was of the order 30 megohms, and one specimen broke down at 1200 volts. The celluloid condensers used in the experiments were found to discharge slowly at first, and after a certain time the deflections of the galvanometer became reversed and attained a steady negative value. This the author attributes to an E.M.F. of about 0·0006 volt between the mercury and celluloid.

Similar experiments on gutta-percha tissue showed no such E.M.F. and the electrification was normal. The resistance usually attained a maximum for voltages between 600 and 800. Although the tissue had a thickness of only 2 mils (0·002") it stood a pressure of 1200 volts and offered a resistance between circular faces 5½ inches in diameter of about 3000 megohms.

The opaque white spots seen in celluloid under the microscope led the author to test the behaviour of mixtures of conducting and insulating materials. A strip of gutta-percha was warmed and coarse brass filings scattered over it as thickly as possible. In spite of this the resistance was practically infinite, even when tested with 750 volts. A number of rods were made from mixtures of brass and gutta-percha in various proportions, and on testing these it was found that if the weight of filings exceeded about twice that of the gutta-percha, the resistance of a rod 20 inches long ⅜-inch diameter was small (sometimes a fraction of an ohm); whereas a slightly smaller proportion yielded rods having resistances measured in thousands of megohms. Such rods were proved to be effected by oscillating discharges in a manner similar to Prof. Minchin's "impulsion" cells and M. Branly's tubes of filings. Experiments were also made on the behaviour of such rods when subjected to high alternating pressures. This caused small local arcs to form along the rods, but did not permanently destroy their high resistance.

In connection with Mr. Appleyard's paper, a "*Note on the Behaviour of certain Bodies in presence of Electromagnetic Oscillations*," by Prof. G. M. MINCHIN, M.A., was read by Mr. ELDER.

Referring to the employment of impulsion cells, metallic films, &c., for detecting the nodes of electromagnetic vibrations, he says that so far the physical state of such bodies are too variable to be of service. Metallic surfaces formed by embedding fine metallic powders in films of gelatin, shellac, or sealing-wax are, as described in a previous communication to the Society, found to act as insulators, but become conducting when subjected to strong electromagnetic disturbances. After a current has once passed through such a film, its resistance is changed by very feeble impulses; whereas previously it failed to respond to strong ones. On breaking contact by removing the electrode from the surface, the film loses its conductivity; the time necessary to do this depending on the hardness of the matrix. The resistance of a film containing tin powder, measured between the rounded tips of two platinum wires 1 c.m. apart, varied under the electromagnetic impulses from infinity to 130 ohms.

In conclusion, the author points out that with films and tubes the whole phenomenon relates to change of resistance; whereas impulsion cells may have currents from external sources passing through them whilst in either the sensitive or insensitive states.

Mr. BRIGHT and Mr. ENRIGHT asked questions as to the

electrification of gutta-percha, and the bridge connections in the resistance tests of the semi-conducting rods respectively, to which Mr. APPLEYARD replied.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 18, April 30, 1894.

Digestion without Digestive Ferments.—A. Dastre.—The author concludes from his experiments that recent albumenoid substances may undergo, without the explicit addition of digestive juices, a series of the same transformations as under the influence of the gastric juice. The condition of the phenomenon is a prolonged stay (of from some days to some weeks) of the albumenoid in the saline solution at the ordinary temperature. The action is more rapid and more complete at 40°, and on exposure to strong light.

Cupric Bromide.—Paul Sabatier.—The anhydrous compound $CuBr_2$ forms black crystals very deliquescent. Their solution heat in water at 12° is +7·9 cal. The hydrated compound $CuBr_24H_2O$ forms long brilliant crystals of the form of a klinorhombic prism. The crystals, whether hydrated or anhydrous, deliquesce in moist air, forming a very dark liquid. In absolute alcohol they dissolve, forming yellowish red solutions. The characteristic reaction of the cupric salts is that with concentrated hydrobromic acid they yield a very intense and brilliant purple colour. This reaction appears even in liquids containing only 1 part of copper in 30,000 parts of water, or 0·0015 m.grm. of copper. It is more sensitive than any of the other quick reactions usually employed for copper.

A Natural Non-saturated Acetone.—Ph. Barbier and L. Bouveault.—The composition of this acetone is $C_8H_{14}O$. It has a penetrating but pleasant odour, and boils at 169°—170° at the ordinary pressure. Its molecular weight is 126.

New Researches on the Influence of Bacterian Associations. Heightened Virulence of some Microbia. Increased Susceptibility.—V. Galtier.—The author's conclusions are:—1. Microbia, attenuated so far that they can no longer produce a fatal malady, if alone may be intensified and rendered virulent if two species are introduced into an organism. 2. The two microbia may flourish side by side, but in general one of them tends to disappear whilst its companion becomes virulent again. 3. If two microbian species are associated, sometimes the one and sometimes the other recovers its virulence according to the manner of their introduction or according to the species experimented upon. 4. Bacterian associations may be utilised in laboratories to obtain in attenuated microbia a return to virulence. 5. They may not only explain the revival of certain epidemics, but they may aggravate the effects of inoculation made with a benign virus. 6. We may foresee that the introduction of a microbe which confers immunity against a given malady may increase the susceptibility for another.

Revue Universelle des Mines et de la Metallurgie. Vol. xxv., No. 3.

Starch Paste for Iodometric Determinations.—Prof. C. Meinecke (*Chemiker Zeitung*).—The author recommends to prepare the paste with the starch of potatoes, sago, arrowroot, or tapioca, and not with the starch of grain, such as wheat or rice. Grain starches give at the end of the operation a violet or even reddish brown colouration, whilst potato-starch gives a pure blue colour.

Journal fur Praktische Chemie. New Series, Vol. xlix., Nos. 8 and 9, 1894.

Action of Diazobenzolchloride and its Homologues upon Cyanacetiethylester.—Franz Krückelberg.—The hypothesis put forward that the *a*-compounds belong to the mixed azo-compounds, and are therefore tantomeres of the hydrazones, has much in its favour, but no decided proof of its correctness has yet been furnished.

Researches from the Laboratory of the University of Freiburg in Breisgau. CXXXVII. Parachlorchinoline.—Ad. Claus and Alf. Schedler.—This memoir does not admit of useful abstraction.

Behaviour of Hydrogen Sulphide with the Sulphone Compounds. A Contribution to the Dependence of Chemical Reactions on the Nature of the Solvent.—R. Otto.—The author proposes the questions whether sulphuretted hydrogen has not alone a reductive action upon sulphonic chlorides, liquid *per se*, or liquefied by the application of heat, or does it require a solvent? In the latter case is the nature of such solvent indifferent or not for effecting the reductive process? We may assume that all the sulphone compounds which can be reduced by nascent hydrogen can also be reduced more or less readily by hydrogen sulphide.

Communications from the Chemical Institute of the University of Kiel. On Pyrazines, together with a Reply to Wolff's Remarks in the *Berlin Berichte*.—C. Stoehr.—This memoir is of a severely controversial character.

Oxidation of some Non-saturated Bromohydrocarbons.—C. H. v. Hoessle.—The author examines the action of dilute alkaline solutions of potassium permanganate upon the bromo-derivatives of ethylene.

Nomenclature of Organic Chemistry.—E. Seelig.—The author does not, as it might have been hoped, propose any remedy for the ultra-sesquipedalian nomenclature of organic chemistry.

MISCELLANEOUS.

On the Fluorine present in Bones and Teeth.—Dr. S. Gabriel.—In the *Zeit. f. Anal. Chemie*, xxxii., 550, E. Wrampelmeyer gives the proportion of the fluorine as fluctuating between 0·65 and 1·40 per cent. He considers that in the experiments of the present writer, which showed in teeth merely traces of fluorine, a loss of fluorine must have occurred.—*Zeit. f. Anal. Chem.*, xxxiii., Part 1.

Practical Encouragement to Science.—From the *Frankfurt Herold* we glean the following significant facts. The Höchst Colour Works (Farbwerke) supply professors at all our universities with materials for experiments at from 20 to 30 marks (shillings) per kilo., whilst their ordinary sale prices may amount to 300 marks! Compare this liability on the part of a trading company with the conduct of our Government with its recent addition of coal-naphtha to methylated alcohol. Further, during the vacation when the laboratories are mostly closed the same company place their own establishments at the disposal of the professors, with all mechanical agencies, and this without any "red-tape" formalities. In encountering such rivalry we, not content with handicapping ourselves with our examinational system of education and the one-sided reciprocity of our patent laws, can scarcely be kept from imposing difficulties in the sale of chemical reagents.

MEETINGS FOR THE WEEK.

Monday, 21st.—Society of Chemical Industry, 8. "A By-Product obtained in Liquidating Copper with Lead," by W. Gowland, F.I.C. "The Manufacture of Smokeless Powder," by Oscar Guttmann, F.C.S.
—— Medical, 8.30. (Annual Oration).
Tuesday, 22nd.—Royal Institution, 3. "The Modern Microscope: an Instrument for Recreation and Research," by the Rev. W. H. Dallinger, F.R.S.
—— Society of Arts, 8. "Decorative Art in connection with Elementary Education," by Selwyn Image, M.A.
—— Medical and Chirurgical, 8.30.
—— Institute of Civil Engineers, 8.
—— Photographic, 8.
Wednesday, 23rd.—Society of Arts, 8. "Liquid Fuels," by G. Stockfleth.
—— Geological, 8.
Thursday, 24th.—Royal, 4.30.
—— Society of Arts, 4.30. "The Commerce of Siam in relation to the Trade of the British Empire," by C. S. Leckie.
—— Royal Institution, 3. "Egyptian Decorative Art," by Prof. W. M. Flinders Petrie, D.C.L.
—— Institute of Electrical Engineers, 8.
—— Physical, 5.
Friday, 25th.—Royal Institution, 9. "The Development of the Astronomical Telescope," by Sir Howard Grubb, F.R.S.
—— Society of Arts, 8. "New South Wales," by J. Inglis, M.L.A.
Saturday, 26th.—Royal Institution, 3. "The Stage and Society," by Robert W. Lowe.

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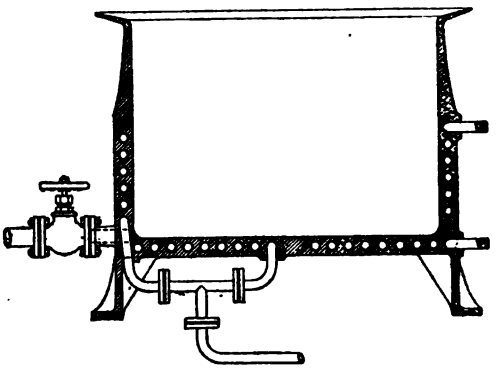

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says:—

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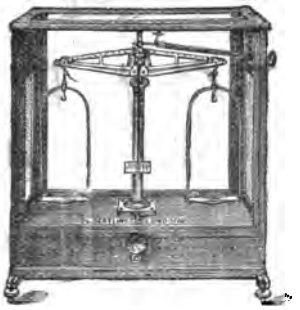

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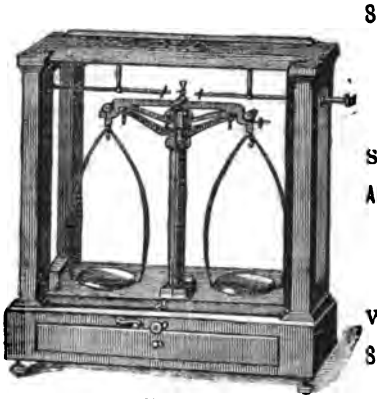

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THE CHEMICAL NEWS.

VOL. LXIX., No. 1800.

MILOSIN, ALEXANDROLITE, AND AVALITE.

By S. M. LOSANITSCH.

MILOSIN and Avalite are Servian minerals the composition of which has not been established. To decide this question I have undertaken the inquiry which has led me to the discovery of a new mineral. All these minerals have also a practical importance, as they accompany the Servian mercury ores.

Milosin was first found by Von Harder in the mountain Rudujak in 1835, and was examined by Breithaupt in 1838 (*Journ. f. Prakt. Chemie*, xv., 327). Von Harder has made this mineralogical journey at the instigation of Prince Milo, and hence he named the new mineral Milosin. The summit of the mountain Rudujak consists of a quartz impregnated with avalite which has penetrated through the serpentine. In the hollows of this quartz we find the Milosin. Subsequently Milosin was found by Avala and Baa in the avalitic quartz of Servia, and abroad it has been discovered on Voltera in Tuscany. In its aspect Milosin is an earthy mass varying in colour from green to blue in several shades.

Breithaupt has merely examined Milosin qualitatively. The first quantitative analysis is due to Karsten (*Pogg. Annalen*, xlvii., 485), and it has since been analysed by Lecco (*Zurick Natur. Gesell.*, xvii., 68), and Blagojevic (*Geol. Ann. der Balkan Halbinsel.*, ii., 72, Servian). According to the analyses of these three chemists the composition of Milosin is—

$$Al_2O_3,SiO_2.3H_2O,$$
$$2Al_2O_3.3SiO_2.4H_2O,$$
$$Al_2O_32SiO_2.2H_2O,$$

in which the equivalent quantity of alumina is replaced by 3 per cent of chromic oxide.

According to the microscopic examinations of Kengot (*Zurich Natur. Gesell.*, xiv., 211) the mass of Milosin consists of a crystalline and an amorphous portion. The crystalline part, according to Kengot, is probably kaolin, $H_2O.Al_2O_3+H_2O.2SiO_2$, and the amorphous Milosin, $H_2O.Al_2O_3+H_2O.SiO_2$, in which a part of the alumina is replaced by chromic oxide.

All these discordant analyses and their small percentage of chrome show that the material analysed was impure.

When I on one occasion obtained a large quantity of Milosin I noticed that the several pieces had different colours between green and blue. This alone indicated that the material were not homogeneous, and by a few approximate analyses I became convinced that the blue fragments were richer in water and poorer in chrome than the green portions. Thus it was easy to see that the material is a mixture of two minerals, one of which is blue and the other is green. In order to obtain these two minerals in a state of purity I sought out the purest blue and green pieces, which I had freed from quartz and other foreign matter by means of the solution of potassium mercuric iodide. In this manner I obtained a blue and a green preparation which on analysis proved to be two distinct mineral individuals. For the blue mineral I have retained the old name Milosin. But the green compound obtained from Milosin I shall designate as Alexandrolite, after the name of Milo's successor, our king Alexander.

Milosin.—Milosin has a bluish grey colour. Under the microscope it appears transparent and crystalline. It loses its water of hydration only on ignition. It is insoluble in acids, with the exception of hydrofluoric acid, in which it dissolves tumultuously. When dried at 130° it consists of—

Silica	76·37
Alumina	30·18
Chromic oxide	9·75
Ferric oxide	0·91
Magnesia	trace
Potassium oxide	trace
Water	13·76
	100·88

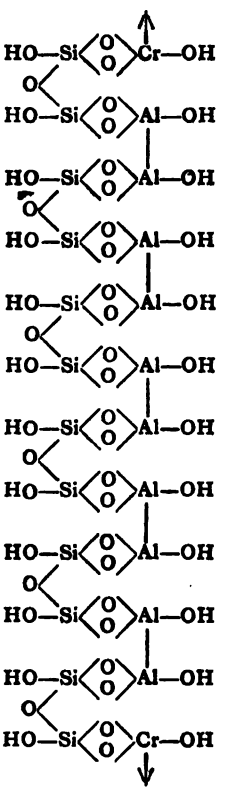
According to these figures we may establish the following formula :—

$$5(5Al_2O_3.2SiO_2.2H_2O)$$
$$Cr_2O_3.2SiO_2.2H_2O,$$

which requires—

$12SiO_2$	= 720	= 45·35
$5Al_2O_3$	= 510	= 31·89
Cr_2O_3	= 153	= 9·56
$12H_2O$	= 216	= 13·51

Hence Milosin is a hydrated aluminium and chromium bisilicate, similar in composition to clay. Its constitution may be represented by the following scheme :—



Alexandrolite.—Alexandrolite has a green colour; it is opaque and probably amorphous. Its water is not expelled below ignition. It dissolves only in hydrofluoric acid. If dried at 130° it gives on analysis—

Silica	52·07
Alumina	20·76
Chromic oxide	13·74
Ferric oxide	2·22
Magnesia	trace
Potassium oxide	trace
Water	10·88
	99·67

According to these figures we may establish the following formula for Alexandrolite :—

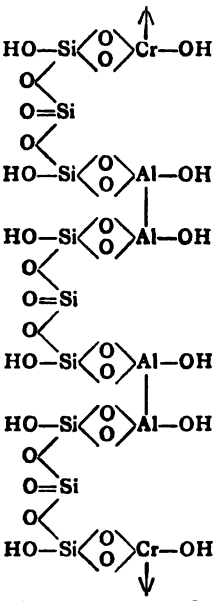
$$2(Al_2O_3.3SiO_2.2H_2C)$$
$$Cr_2O_3.3SiO_2.2H_2O,$$

which requires—

$$9SiO_2 = 540 = 53{\cdot}73$$
$$2Al_2O = 204 = 20{\cdot}30$$
$$Cr_2O_3 = 153 = 15{\cdot}22$$
$$6H_2O = 108 = 10{\cdot}75$$

A slight admixture of Milosin may explain this discrepancy between theory and analysis.

Alexandrolite is therefore a hydrated aluminium and chromium trisilicate, and its constitution is the following :—

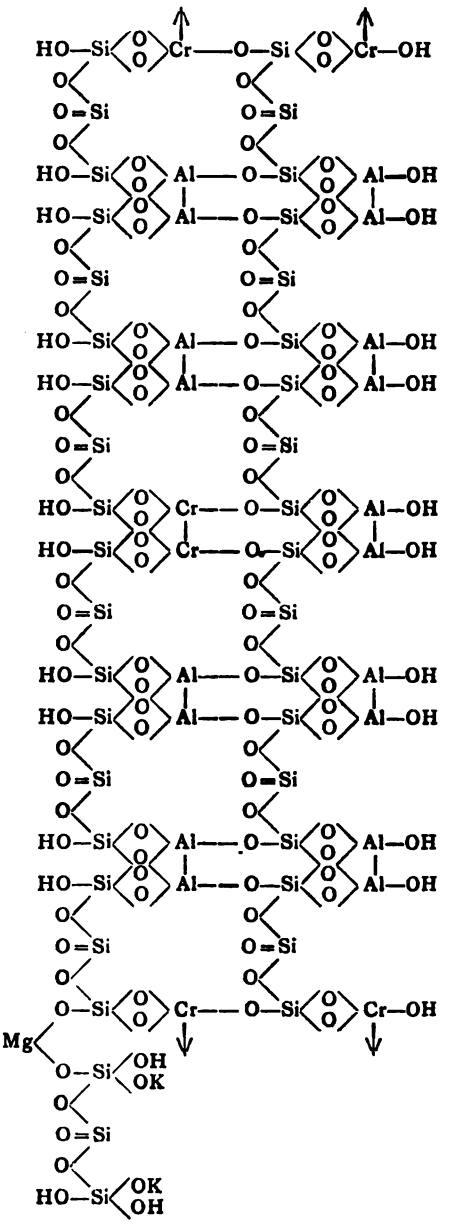


When I analysed avalite for the first time (*Berichte Deutsch. Chem. Gesell.*, xvii., 1774), the preparation was impure, whence I was unable to deduce a formula from the results. Now I am enabled not merely to submit the composition of this interesting mineral, but to give some details as to its occurrence and its genetic connection with Milosin and Alexandrolite.

Avalite occurs in Servia as an associate of quartz and dolomite, which are more or less strongly impregnated with this mineral, so that they are coloured green. Such avalitic quartz is, with us, very widely distributed in the serpentine, passing through the entire region in three parallel bands in the direction from north to south. Along with such avalitic quartz there are found on the Avala large masses of avalitic dolomites. These avalitic quartz and dolomites are characterised by carrying mercury ores. I will merely mention that the mercury ores on the Avala are embedded in such quartz and dolomite, and also that in many other avalitic quartzes there occur traces of cinnabarite.

According to a private communication from J. Mactear, the Mexican mercury ores of Guadalcasar are likewise embedded in avalitic quartz which has penetrated through the serpentine. Hence it seems that avalite and cinnabarite are intimately connected.

The richest material for the separation of avalite is the green avalitic earth which is found in the mercury mine "Avala." This earth contains both an earthy and a crystalline avalite, mingled with sand, chromite, cinnabarite, limonite, &c. The earthy variety of avalite can be separated from this material by elutriation in a state of approximate purity. Crystalline avalite can, however, not be entirely freed from quartz, as both have the same specific gravity.



Earthy avalite has a light green colour, and the crystalline form is of an emerald green. The earthy variety, if moistened, gives off the same smell as moistened clay. Both forms of avalite lose their water if ignited and turn brownish. The mineral is not affected by acids, except hydrofluoric acid, in which it readily dissolves. If dried at temperatures exceeding 100° and washed with hydrochloric acid, it yields on analysis the following results :—

Silica	54·66
Alumina	20·46
Chromic oxide	10·88
Ferric oxide..	1·18
Magnesia	2·06
Potassium oxide	4·61
Water	5·66
	99·51

which correspond to the following formula:—

$$9(Al_2O_3.3SiO_2.H_2O)$$
$$3(Cr_2O_3.3SiO_2.H_2O)$$
$$MgO.2K_2O.3SiO_2.H_2O,$$

as it requires—

$39SiO_2$	$=2340=$	56·0
$9Al_2O_3$	$=918=$	22·0
$3Cr_2O_3$	$=459=$	11·0
$2K_2O$	$=188=$	4·0
MgO	$=40=$	1·0
$13H_2O$	$=234=$	5·6

Avalite is therefore a hydrated tri-silicate. If we consider the facts that Milosin and Alexandrolite are potassiferous, and that these three minerals occur together, we can assume with a certain probability that Milosin and Alexandrolite have been formed by the decomposition of avalite—

$$9(Al_2O_3.3SiO_2.H_2O)$$
$$3(Cr_2O_3.3SiO_2.H_2O)$$
$$MgO.2K_2O.3SiO_2.H_2O + 19H_2O =$$
$$5(Al_2O_3.2SiO_2.2H_2O)$$
$$(Cr_2O_3.2SiO_2.2H_2O)$$
$$+ 2\left\{\begin{matrix}2Al_2O_3.3SiO_2.2H_2O \\ Cr_2O_3.3SiO_2.2H_2O\end{matrix}\right\}$$
$$+ MgO.2K_2O.3SiO_2.2H_2O + 6(SiO_2H_2O)$$

A constitution of avalite representing this decomposition is shown in the subjoined scheme (see preceding column).

Chemical Laboratory of the
High School of Belgrade.

VACUUM WATER-BATH FOR TEMPERATURES OF 100° C. AND UPWARDS:

With Note on Estimation of Moisture in Syrups.

By J. BAUMANN, Ph.D., and WILLIAM HORN.

Chemists, and especially those who have many syrup analyses to make, find difficulty in their determinations of moisture in low sugars containing much invert sugar, syrups, and saccharine liquids generally. This is caused by the fact that the above substances, when placed in the water-bath to dry, take so long, and being subjected to a high temperature for about twenty-four hours, they are in danger of being partially decomposed.

It may be taken for granted that the results obtained by means of the ordinary water-bath are not reliable.

To overcome this, Dr. Herzfeld, of Berlin, introduced his toluol vacuum bath, and by substituting toluol for water he found that the inner chamber was kept at a constant temperature of 107° to 108° C.

The results with syrups and molasses got in this bath were very satisfactory, the syrups being completely deprived of their moisture in about four hours. However, the toluol bath has this objection, that extreme care has to be taken to condense all the vapours from the bath owing to their inflammability; and even though condensation is effectually carried out, any leak in the sides of the bath is apt to cause fire unless watched.

We have devised the following bath, with which we get the same results and which can be used at pleasure to obtain a temperature of 100° C. or any temperature above that point, the maximum temperature being limited only by the strength of the material used. The bath is composed of strong copper and is cylindrical in form. The inner chamber is 10 inches long and 4 inches in diameter, and is fitted with a perforated shelf about 1 inch below centre. The outer chamber is 6 inches in diameter and 11½ inches long, and is fitted with a very well ground safety valve (weighted) and a gauge glass at end to see level of water. There are two tubes connected with the inner chamber, but having no connection with the outer. The one is used for placing an indiarubber cork with thermometer, and the other is connected on the outside of the bath with a three way tube. On top of three-way tube is placed a vacuum gauge with a stop-cock. Stop-cocks are placed on each of the other arms, the one being used for connecting with a Körting aspirator, and the other with the air.

It is advisable to have the suction pipe, which is connected with the three-way tube, carried to the back of the inner chamber and underneath the perforated shelf. If this were not done the inrush of air when the stop-cock on the outside is opened to the atmosphere would blow out some of the contents of the capsules containing the moisture quantities.

The shelf in the inner chamber must be made so that it can pull out.

The front of the bath is made of thick cast brass, and is fitted with a movable iron clamp which is used for tightening up the thick glass cover against an indiarubber ring placed between glass and brass front. This iron clamp is not actually necessary, as the vacuum usually holds the glass quite tight against the bath.

To use the bath, water is placed in the space between the inner and outer chamber and heat applied. As soon as it is boiling the safety valve is closed and the weight placed on the arm. By moving the weight along the arm of the valve the water can be made to boil at any pressure wished, and consequently at any temperature above 100° C.

By experience we find that the best arrangement for a sugar laboratory is to have a bath which will stand a pressure of about 10 lbs., and by this, of course, we get a temperature at anything between 100° and 115° we want. By making the bath of stronger material and having a heavier weighted valve a much higher temperature can be got.

The advantage of this bath over the toluol bath is this, that one can alter the temperature to any degree over 100° C. and have no danger of fire; and the advantage over the ordinary water-bath is the fact that it can be used as an ordinary bath, or by connecting one of the limbs of the three-way tube with an aspirator either a partial or almost complete vacuum can be obtained.

In estimating the moistures in syrups with this apparatus it is advisable to place the capsules in the bath when it is almost cold, then, after fixing on the glass cover and putting on the vacuum pump or aspirator, start to heat the bath. When it is boiling note the time and weigh capsule three hours afterwards. Replaced in the bath, after another hour the capsule has either the same weight or has only lost about 3 or 4 m.grms. It is usually constant in weight in four hours.

As regards the capsules they are best to be made of nickel, and about 2½ to 3 inches in diameter and ½ inch deep.

To insure correct results with syrups take coarse sand which has been passed through a sieve 10 meshes to the inch and remaining on sieve 20 meshes to the inch, treat the sand with strong hydrochloric acid, then wash well, and ignite in large graphite crucible and pour while hot into a stoppered bottle, and keep for future use.

Having prepared the sand, take a 2½ inch capsule and place in it 15 grms. or thereby of the sand, dry in water-bath at 107° C., cool in desiccator, and weigh; then drop about 2 grms. of syrup on top of sand and weigh. Warm the capsule and mix exceedingly carefully and well the sand and syrup by means of a glass rod previously weighed with the capsule, then place in water-bath, and dry as described in complete vacuum at 107° C.

Note.—It is advisable from time to time to test the water-bath with water to see that it is capable of standing the required pressure. This can easily be done by filling the bath completely with cold water, and connecting it by means of a strong I.R. tube with the water main. The

water is then turned on and the pressure measured either by a spring or mercury gauge.

Laboratory of
Roxburgh Street Refining Co., Greenock,
April, 1894.

EXPERIMENTS ON IMMUNITY AGAINST ASIATIC CHOLERA.

By P. TSIKLINSKY.

This article is mainly a review of the results obtained by M. Issaef in his experiments on vaccination against cholera. These results are to a certain extent remarkable, as they do not agree with our usual ideas on the subject.

M. Issaef's first experiments were to inoculate a number of guinea-pigs with the *minimum* fatal dose of cholera virus; some of these had been protected by previous vaccination with infected blood, while the others had not. He found, as he expected, that the former required much larger doses to kill them than did the latter; but in continuing his experiments he also found that the bactericidal properties of blood taken from vaccinated guinea-pigs or from persons who had had cholera was hardly any greater than that of blood from a normal healthy person. In order to try and find the reason of this action, he made a number of experiments with healthy persons and also with those who had suffered not only from cholera but from other maladies, such as typhoid, pneumonia, &c. He found at length that the degree of insensibility of the animal to cholera virus is in direct relation to the quantity of serum injected, but it is advisable not to go beyond doses of 1 c.c. or 1·5 c.c.

This protective power of healthy blood is one which is not yet explainable, and about which we can only bring forward hypotheses. Moreover, it is not only the blood, and the secretions in general, of healthy persons which protects guinea-pigs from cholera, but other liquids, such as the physiological solution of sodic chloride, soup, and a 2 per cent solution of nucleine.

These experiments led to the following conclusions, viz.:—1. That the above-mentioned liquids will give immunity provided that they are not very toxic. 2. That the resistance thus acquired is temporary, and, while getting gradually weaker, disappears after four or five days. 3. The protective liquid should be inoculated twenty-four hours before the infection (the time of greatest resistance). 4. The protective power of different liquids varies considerably, the most feeble being sodic chloride, then coming urine, soup, normal blood, and 2 per cent nucleine.

As for the serum of animals vaccinated against cholera, M. Issaef states they give guinea-pigs a considerable degree of resistance, but that this depends on the time which has elapsed since the vaccination. Thus it is useless until about the seventh day, and attains its maximum strength a fortnight after the operation, after which it gradually disappears.

These and other experiments brought M. Issaef to the opinion that the cause of the protective power was to be found in the action of the cellular tissues. He therefore made fresh experiments, and by examining the discharge from injection punctures and the blood, for forty-eight hours after the injection, found that at first the number of leucocytes diminishes rapidly until after three or four hours, when they commence increasing, and attain their maximum after about twenty-four hours. The intensity of the cellular reaction depending on the properties of the injected liquid and its quality. This reaction is above all most pronounced after injecting the serum of a vaccinated animal, or of a person who has had cholera. The preliminary negative action in this case is so short as to escape observation, while the accumulation of phagocytes commences a few moments after the injection, and attains its maximum after twenty-four hours. After having shown that the injection of different substances gives rise to a state inimical to cholera at the same period as the cellular reaction, M. Issaef attempted to determine the relationship between these two phenomena, and found that with fatal doses of virus, the bacilli multiplied very quickly, while the leucocytes at the same time disappeared; but with a maximum *non-fatal* dose, at the end of seven hours, the picture changed, the number of bacilli commenced to diminish rapidly, while the leucocytes increased with corresponding energy. In fourteen hours the phagocytes reached their maximum, while free bacilli became extremely rare, disappearing entirely after about thirty-six hours.

M. Issaef's work is of great interest, showing as it does the great importance of the natural forces of our organism to the favourable issue of an illness. The combat is waged by the elements of the blood, and notably by the white corpuscles; thus, those substances which stimulate their activity contribute by that means to the curing of the patient; and, further, although soup is an excellent medium for cultivating cholera germs, it at the same time serves for their destruction by its stimulating action on the phagocytes.

This research shows plainly that it is substances capable of exciting this activity of leucocytes which ought to give rational therapeutic methods of combating disease. —*Revue Générale des Sciences Pure et Appliquées*, April, 1894.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending April 30th, 1894.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, May 8th, 1894.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined two were recorded as "clear, but dull," and one as "slightly turbid." The remainder were clear, bright, and well filtered.

The rainfall in the Thames valley during the month of April has come very close to the average. The actual fall at Oxford has been 1·7 inch, whilst the average for twenty-five years is 1·78 inch, showing a deficiency of only 0·08 inch. The rain has been pretty evenly distributed over the month, the second half being a little wetter than the first half, but the downfall has come in the form of gentle showers, which soak into the ground and do more good than twice the amount of rain, falling at longer intervals, and rushing over the land to the nearest water-course to the sea.

The Thames-derived waters are now of a high degree of purity, and may be considered to have assumed their summer characteristics. Active vegetation, increasing temperature, and abundant light promote oxidation and reduce the dissolved organic matter to a low point, while the lowering of the brown constituent in the colour-meter is a further proof of the diminishing amount of organic carbon present.

The following comparison between the different constituents in the March and April waters will show the changes since our last report.

Averages of the Five Supplies Derived from the River Thames.

1894.	Common salt per gallon.	Nitric acid per gallon.	Hardness, degrees.	Oxygen required per gallon.	Organic carbon per gallon.	Organic carbon per gallon.	Colour. Brown. Blue.
	Means.	Means.	Means.	Means.	Means.	Maxima.	Means.
Mar.	2·285	1·101	15·32	0·052	0·121	0·162	21·3 : 20
April	2·100	0·995	15·00	0·034	0·076	0·108	14·2 : 20

We are, Sir,

Your obedient Servants,

William Crookes.

William Odling.

A POWERFUL AND EASILY CONSTRUCTED REFRIGERATOR.

By H. N. WARREN, Research Analyst.

To procure ice in the laboratory, even when intended to illustrate the same as an experiment, is generally brought about either by the clumsy method of mixing large quantities of the original compound with sodium or calcium chloride, and exposing to its influence the substance under examination; or, when in larger quantity, by employing one of the costly refrigerators now upon the market. With a practical chemist all such apparatus is ridiculed. Take for the expensive refrigerator a fractional distillation flask; place the flask in the desired quantity of water which is intended to freeze, contained in a suitable receptacle. Through the neck of the flask is now inserted a rubber tube terminating in a glass point, which should all but touch the surface of the liquid contained in the flask, which consists of about 20 c.c. of an equal mixture of ether and carbon disulphide. The further end of the rubber is now connected to a pair of constant bellows, and a brisk current of air continued for about three minutes; almost immediately the thermometer will sink to zero, the vapour of the mixture introduced escaping through the small tubular of the flask, whilst the outside vessel, containing the water, will be found to have become inseparable owing to the thickness of the ice formed. This constitutes a beautiful experiment for a lecture table, where the gradual development of the ice can be readily observed. By this means I have frozen a litre of water when the room was at 70° F. in half an hour.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

Chemical Chair at South Kensington.—Prof. T. E. Thorpe, in consequence of his appointment as chief of the Chemical Department of the Inland Revenue, has resigned the Chemical Chair at South Kensington. He will be succeeded by Dr. W. A. Tilden, F.R.S., who will commence his duties in October next. His able guidance of the Institute of Chemistry emboldens us to hope that he will prove no less successful at South Kensington. We hope that Dr. T. E. Thorpe, F.R.S., in his new sphere of activity will not fail to see the absurdity of the addition of mineral naphtha to methylated spirit and to act upon his conviction.

THE METHODS OF SUGAR ANALYSIS.*

(Concluded from p. 234).

Estimation of Sucrose.

(*a*) *In Sugars, Massecuites, &c.*—Take the normal weight in tared dish for the instrument employed; wash into a 100 c.c. flask; add water until volume is 80 to 85 c.c. When the crystals are all dissolved add sufficient lead acetate to throw down all precipitable matter. With molasses and massecuites add sufficient acetic acid to convert the sub- into the neutral acetate. Make up to mark, using a little ether spray to dissolve bubbles; filter, throwing away the first 10 to 15 c.c.; place in observation tube and polarise. If too dark to read filter through finely-powdered dry bone-black, rejecting the first 30 to 40 c.c.

For adjusting the polariscope, graduating flasks, &c., the method of the United States Bureau of Internal Revenue, adopted last year, was continued. (See *Bull.*, xxxi., pp. 228—232).

(*b*) *In Juices, &c.*—Transfer, by means of a pipette, to the tared sugar dish the normal, or multiple normal, weight of the juice or syrup to be analysed.

In the case of juices and thin syrups, the contents of the dish are at once washed into the 100 c.c. flask.

The solution in the flask is made up to 80 or 90 c.c., and the least amount of basic lead acetate solution sufficient to decolourise the contents is added. The solution is then made up to the 100 c.c. mark and thoroughly shaken before filtering. In case much foaming and bubbling takes place, rendering gauging difficult, the addition of a few drops of ether is found advantageous. The solution is then poured upon a dry filter and the filtrate is collected in a dry beaker, the first portions to pass through being rejected. If it is found impossible to obtain a perfectly clear filtrate, it may be necessary to decolourise with dry powdered bone-black either mixed with the liquid itself or placed upon the filter.

In case of dark-coloured products, the addition of alumina cream immediately after the lead sub-acetate is quite advantageous, the quantity of the former employed being in excess of that of the latter. For many sugars the use of alumina cream alone will produce a satisfactory clarification. Where double polarisation is employed, acetic acid should be added to the filtrate used for the direct reading in sufficient proportion to break up the compound of lead and levulose which has been formed.

Preparation of Lead Sub-acetate Solution.—Boil an aqueous solution of lead acetate with an excess of lead oxide (PbO) for half an hour, and make filtered solution of a concentration of not less than 1·25 specific gravity. Solid sub-acetate of lead may be substituted for the normal salt and oxide in the preparation of the solution.

Alumina Cream.—Prepare a cold saturated solution of alum in water and divide into two unequal portions. Add a slight excess of ammonium hydrate to the larger portion, and then add by degrees the remaining alum solution until a faintly acid reaction is secured.

Optical Method by Inversion.—For raw sugar, molasses, &c.

(*a*) *Method of Clerget.*—Make up the solution as above and place 50 c.c. of the filtrate in a flask marked at 50 and 55 c.c. Fill to the upper mark with pure fuming HCl and mix well; place in water and heat until the thermometer, with the bulb as near the centre of the sugar solution in the flask as possible, marks 68°, consuming about ten minutes in the heating; remove, cool quickly to room temperature, and polarise, noting the temperature. If the sample contained originally any invert sugar, the second polarisation should be made at approximately the same temperature as the first. The percentage of sucrose is then calculated by the following formula:—

* Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (American) at its Meeting at Chicago, August, 1893.

S = percentage of sucrose.
a = first polarisation.
b = second polarisation (usually to the left).
$a \pm b$ = sum of the polarisations.
t = temperature of observation.

Then—

$$S = \frac{a \pm b}{144 - \frac{t}{2}}$$

a and b are to be added when of different signs and the difference taken when of the same sign.

(*b*) *The Official German Method* may be used as follows:—26·048 grms. are dissolved in a sugar flask and the solution made up to 100 c.c.; 50 c.c. of this solution are transferred by means of a pipette to a 50 or 55 c.c. flask, cleared, and polarised, the reading being corrected for the extra 5 c.c. The liquid adhering to the pipette is washed into the 100 c.c. flask containing the remaining 50 c.c. (13·024) grms.), 5 c.c. of concentrated hydrochloric acid (38 per cent, specific gravity 1·18 at 15°) added, and the flask heated for fifteen minutes at 67° to 70° in a water-bath. The temperature should not exceed this limit. The flask is then cooled rapidly and the solution made up to 100 c.c. If the liquid is coloured it is shaken with ½ to 1 grm. of bone-black and filtered through a double filter. It is then polarised in a 200 m.m. tube which is provided with a thermometer. As the rotatory power of invert sugar is much influenced by the temperature, this factor must be regarded. The reading is best taken between 18° and 22°, and the temperature accurately determined. The reading must also be doubled on account of the dilution of the liquid.

To calculate per cent of sucrose (R) the two readings are added together, the sum (S) multiplied by 100 and divided by $142{\cdot}4 - \frac{1}{2}t$, where t is the temperature at which the invert reading was taken. If the temperature is exactly 20° the result can be made more accurate by substituting 142·66 for 142·4; thus—

$$R = \frac{100\ S}{146{\cdot}66\frac{1}{2}} = \frac{100\ S}{132{\cdot}66} = 0{\cdot}7538\ S.$$

If very much invert sugar is present, both the direct and indirect readings must be taken at the same temperature.

(*c*) *Method of Lindet.*—Place 50 c.c. of the filtrate as above in a flask marked at 100·5 c.c., add 5 grms. of powdered zinc (zinc dust), place in boiling water, and when at the boiling-point add, little by little, 5 c.c. of strongest HCl. After the acid has all been added, cool and make up to mark. Polarise in a 400 m.m. tube, or multiply the reading in a 200 m.m. tube by 2. Calculate the percentage of sucrose as before.

(*d*) *Gravimetric Method.*—Determine first any reducing sugar in the sample, then invert sucrose, neutralise free acid, and re-determine the reducing sugar. Deduct the percentage of reducing sugar obtained at first, and the remainder will be reducing sugar derived from sucrose; multiply this number by 0·95 to obtain the percentage of sucrose in the sample.

A Novel Carbon Chloride: Hexachloric Benzene Bichloride.—Et. Barral.—On causing phosphorus pentachloride to react upon hexachlorophenol, C_6Cl_6O, the author has replaced the oxygen by Cl_2 obtaining hexachlorobenzene bichloride. Hexachlorophenol and phosphorus pentachloride heated to 150°—155° in a sealed tube for twenty-four hours yield a yellowish solid mass, from which he has isolated hexachlorobenzene, small white micaceous crystals, insoluble in benzene, but very soluble in ether. This substance, probably an organic phosphorus compound, is still under examination. It is a yellowish oily matter of an odour like that of the chloroquinones, and forms long colourless crystals melting at 159° to 160°. The author is continuing the examination of these compounds.—*Comptes Rendus*, cxviii., No. 19.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 3rd, 1894.

Dr. ARMSTRONG, F.R.S., President, in the Chair.

MESSRS. R. L. Jenks and John McKillop were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Arthur Hadley, 226, Monument Road, Edgbaston, Birmingham; G. L. Parker, The Paddocks, Eccleston, Chester; John F. Rolfe, Homewood, Leytonstone, Essex; Herbert John Taylor, Fern Villa, 33, Russell Street, Eccles, near Manchester; Charles H. H. Walker, Prospect Place, Cainscross Road, Stroud.

The following were elected Fellows of the Society:—F. E. Alhusen, Joseph Beynon Ashcroft, Samuel Bernard Asher-Aron, Charles Henry Ashdown, Harry Bowes, Robert William Buttemer, Thomas Chambers, George Hugh Gabb, Arthur Robert Golden, Oswald Ernest William Hewitt, Charles T. W. Hirsch, Edwin James Jackman, Alex. Mitchell Kellas, William Albert Knight, John Abraham Kelly, James Mansell, Charles McMullan, Matthew A. Parker, Thomas John Roberts, Fredk. Wallis Stoddart, James Swinburne, Edwin Terry, Henry L. Wheeler.

Of the following papers those marked * were read:—

*11. "*The Structure and Chemistry of the Cyanogen Flame.*" By ARTHUR SMITHELLS, B.Sc., and FRANKLAND DENT, B.Sc.

The flame of cyanogen burning in air consists of two distinct regions—an inner cone of a bright peach-blossom tint and an investing mantle whose colour shades off from a deep blue to greenish grey.

The authors have endeavoured to ascertain the chemical changes that occur in different parts of the flame by the means employed by Smithells and Ingle for the flames of hydrocarbons (*Trans.*, 1892, 204).

When cyanogen is burnt in the cone-separating apparatus and sufficient air is added, a separation takes place corresponding in colour to the two-coned structure of the original flame. A slight increase in the supply of air causes the inner cone to become bluer and the outer cone greener, whilst a further increase extinguishes the outer cone.

The authors have made a series of analyses of the interconal gases produced in the flame under varying conditions. These analyses show—(i.) The separation of the cones of a cyanogen flame is possible in the apparatus used when the ratio of air to cyanogen is 3·3 : 1 (*i.e.*, about one-third of the amount necessary for complete combustion), and the cones remain intact until the air supply is increased to twice this amount. After this the interconal gases become so diluted with carbon dioxide and nitrogen that they can no longer burn in a second cone. (ii.) When cyanogen is burning in the apparatus with the addition of the minimum quantity of air necessary for the separation of the cones, carbon monoxide is practically the only oxidation product. (iii.) A small quantity of carbon dioxide is formed in the interconal gases. As the air supply is increased the quantity of carbon dioxide increases until it amounts to about half the volume of the accompanying carbon monoxide. (iv.) The interconal gases contain unburnt cyanogen amounting in the case of the minimum air supply to 7½ per cent, and diminishing in quantity to *nil* as the air supply is increased. (v.) Small and variable quantities of oxides of nitrogen are obtained in the interconal gases. (vi.) A variation in the dimensions of the apparatus makes no important difference in the results.

The authors consider that their results are in accordance with Dixon's as to the rate of explosion of cyanogen, which showed that the highest rate corresponds with

oxidation of the carbon to carbon monoxide. They conclude that the inner cone of the ordinary cyanogen flame is determined by the formation of carbon monoxide, and the outer one by the combustion of the carbon monoxide.

The outer cone of a cyanogen flame is not suppressed even when the cyanogen and air have been carefully dried, and this might seem to conflict with the view that it is due to the combustion of carbon monoxide. The authors, however, have shown that the outer cone can be extinguished by drying the gases, provided that it is not too near the inner cone. As it is brought nearer to the inner cone, a point is reached where the temperature of the carbon monoxide is sufficient to ensure its combustion in spite of the dryness of the gases. These results are in harmony with Dixon's observations.

The authors have not found any evidence of the direct combustion of the nitrogen of cyanogen within the flame; their observations go rather to show that oxides of nitrogen are formed on the exterior where they produce a characteristic greenish tinge.

*12. "*The Results of Measurements of the Freezing-Points of Dilute Solutions.*" By HARRY C. JONES.

This is a reply to Pickering's recent criticisms (*Trans.*, li., 293) of the author's work. When the results of Pickering, Loomis, Raoult, and the author on the freezing-points of dilute cane-sugar solutions are compared, differences are seen to exist which at present are inexplicable. It may be possible that the different workers have measured slightly different points of equilibrium. Notwithstanding such differences, Pickering states that when Raoult's, Loomis's, and his own results are plotted as curves they "form figures almost identical."

Pickering's method of manipulating results in his curves, which consists in subtracting a constant multiple of the strength from the depressions, and plotting the number thus obtained ($D-xm$) against the strengths (m), instead of plotting the depressions directly, involves the following errors:—

I. It changes the relations between the freezing-point lowerings found experimentally, without changing the relations between the concentrations.

II. It magnifies all errors; and,

III. It magnifies them differently in different parts of the curves.

The true curves for sulphuric and phosphoric acids were drawn and compared with Pickering's curves from the same results, illustrating the manner in which Pickering obtains the "breaks." The curves which Pickering drew from the author's results by his method involving the above-mentioned errors were shown, by comparison with the true curves, to bear no direct relation to the results.

The tables which Pickering prepared from the results of others in order to throw doubt on the correctness of the author's results would equally justify exactly the opposite conclusion, if he had dealt with actual instead of manipulated differences.

DISCUSSION.

Mr. PICKERING said that all Mr. Jones's arguments were beside the point, for the comparison which he had made of Mr. Jones's results with those of other observers were made by calculation from the *unaltered* experimental values without the use of any plottings whatever (*Trans.*, p. 303, line 32, *et seq.*). Nor were Mr. Jones's arguments valid even against those diagrams, the peculiarities of which led him to make this comparison. His first argument was founded on a fundamental misconception of an elementary fact in geometry—the fact that an alteration in the ratios of the ordinates does not necessarily involve an alteration in the nature of a curve—and the other two were due to a thorough confusion between actual and percentage errors, and between the operations of subtraction and multiplication. The experimental error, being an inseparable portion of the experimentally observed depressions, the former cannot become multiplied unless the depressions themselves are multiplied also, but $D - xm$ represents an operation of subtraction from, and not multiplication of, the depressions (D). An error of a given magnitude is represented by a definite space uniformly throughout the $D-xm$ figures, just as much as it is in the direct plottings of D.

The proof that the subtraction of xm does not alter the nature of the curve is perfectly simple. If the depressions are proportional to the strength of the solutions (m), we shall have $D=xm$ in the direct plotting, and—

$$D' = (a + x)m$$

in the other, both of which represent straight lines: if the depressions are not proportional to the strength, then the plottings will form a curve; but the nature of a curve at any point, m_2, depends on whether the ordinate at that point is greater or less than the mean of two ordinates at points m_1 and m_3, equidistant on either side of it, *i.e.*, whether—

$$BB' \gtrless \tfrac{1}{2}(AA' + CC');$$

in the curve obtained by plotting the values $D-xm$, the nature of the curvature will depend on whether—

$$BB' - xm_2 \gtrless \tfrac{1}{2}(AA' - xm_1 + CC' - xm_3),$$

but since $m_2=\frac{1}{2}(m_2+m_3)$, this expression is identical with the former; any breaks, waviness, or other singularities which exist in the one figure must necessarily exist in the other.

Since the $D-xm$ figures show waviness, it is certain, therefore, that the direct plottings of D must show waviness also, and even on the very restricted scale of the accompanying diagram this waviness is clearly visible. Straight lines have been drawn against the figures to assist the eye in judging their form: with a similar assistance, the waviness of Mr. Jones's results may easily be seen in the drawings of them which he has given in the *Phil. Mag.*, Dec., 1893.

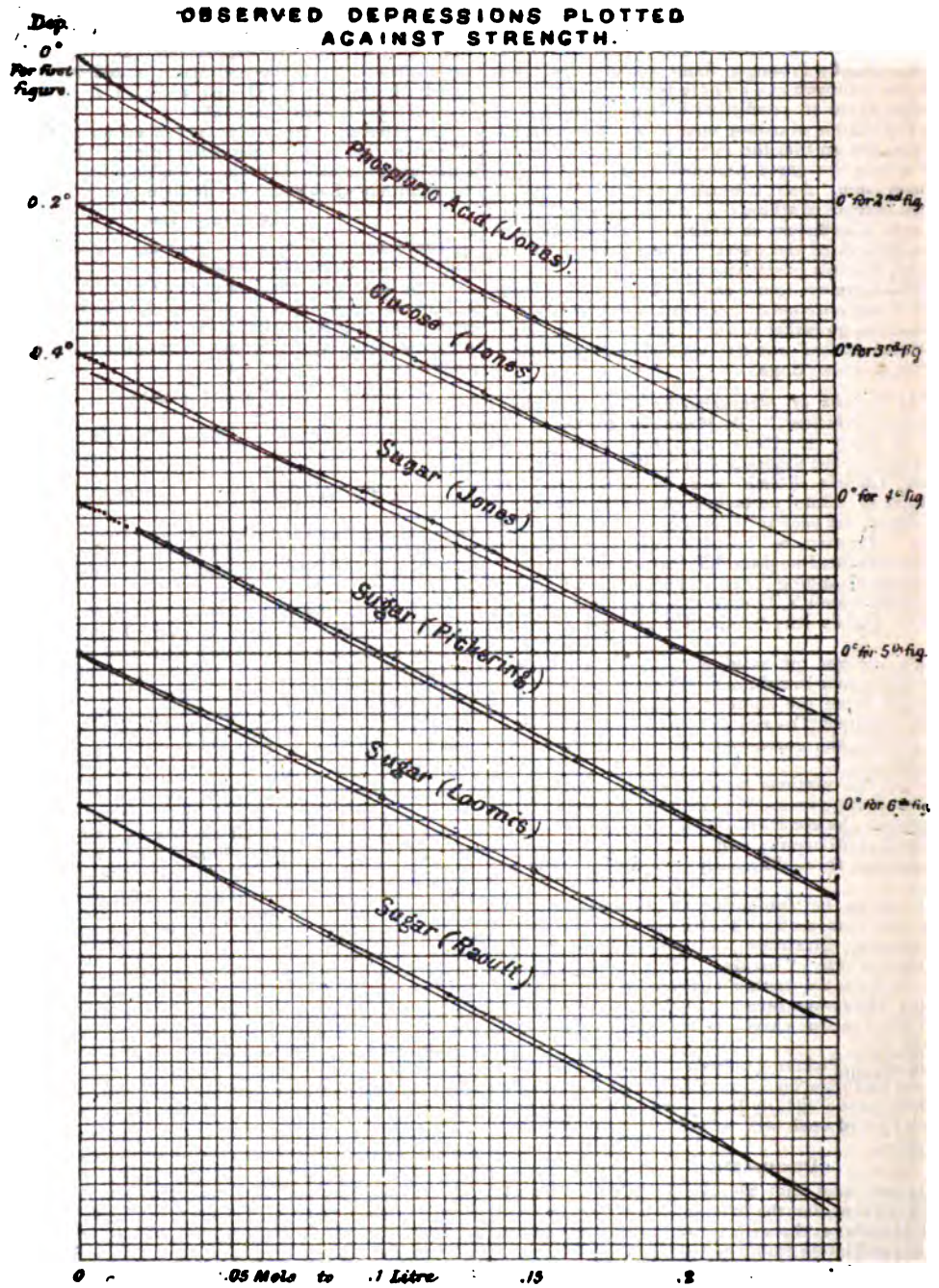
Their waviness can be proved equally well without the use of any diagram: it is only necessary to compare his values with those calculated for a properly-selected straight line, and it will be found that they cut this line at three points, and therefore must form a wavy figure. The line $x=0{\cdot}195m$ is a convenient one to take for Mr. Jones's results with cane sugar, the waviness of which will then be found to depend on differences (errors) of as much as 0·015°.

The values shown by Mr. Jones for portions of the results obtained by different workers with cane-sugar are sufficient to indicate the discrepancy between his results and theirs, for whereas an accumulated error of 0·0019° or 0·0016° would reduce to rectilinarity this part of the results of Pickering, Loomis, and Raoult, it would require errors of 0·006° to obliterate the curvature of Mr. Jones's results. But the exceptional character of the latter can be satisfactorily seen only by comparing the whole series at our disposal; this has been done roughly in the last four figures of the accompanying diagram.

Dr. JAMES WALKER said that he understood Mr. Jones to take objection not to Mr. Pickering's observation that his curves possessed a wavy character, but merely to the distortion of these curves which resulted from the method of treatment adopted by Mr. Pickering in his diagrams. If the depressions of freezing-point had been strictly proportional to the concentrations instead of only roughly so, then, of course, no distortion would have resulted.

Mr. E. H. HAYES explained from the mathematical standpoint the precise relation between the figures obtained by the ordinary plotting preferred by Mr. Jones, and by the modified plotting which was necessarily adopted by Mr. Pickering in order to make the experimental error and the irregularities of the "lowering" easily visible on a diagram of moderate size.

Whichever plotting was used, a temperature error of



given magnitude was represented by the same length, whatever the strength of the solution might be. Taking an ordinary plotting, and drawing a straight line through the origin, the ordinates ($D - xm$) of the modified plotting were simply the difference between the ordinates (D) of the ordinary plotting and those of the straight line (xm) at the same strengths. (Mr. Pickering had, of course, obtained the values of $D - xm$ by calculation and not by measurement). If the two plottings were drawn together on the same scale, and the plane of one of then turned round the temperature axis through any angle, the lines joining corresponding points on the two curves were all parallel, that is to say, either curve was the projection, or, in more popular language, the shadow of the other, a simple mathematical fact which absolutely annihilated the claim of Mr. Jones that the irregularities discovered by Mr. Pickering were introduced by his method of plotting, and that the curves obtained by the latter bore no direct relation to the experimental results. An ordinary plotting, if mathematically correct, would of necessity contain any

such singularity as a waviness or a break if such appeared in the modified plotting, although the steep slope of the curve in the former and its far greater length would prevent them from being as conspicuous. On an unmodified plotting on the same scale as Mr. Pickering's published diagrams, the temperature ordinate for a lowering of 0·32° would have a length of about 10 in. If the observed lowering were strictly proportional to the strength, the experimental points in the ordinary diagram would lie, on the average, evenly about a straight line, and, therefore, since the shadow of a straight line was a straight line, would lie evenly about a straight line in the modified diagram, from which it followed that the modified plottings exhibited by Mr. Jones proved conclusively either the existence of extremely serious errors, or that in the cases chosen for illustration, the lowering varied in a highly complex manner, the irregularities, though small as compared with the total depression, being large as compared with the estimated experimental error.

Mr. Jones had pointed out three details in which the modified plotting differed from the ordinary one.

(1) That it changed the relation between the lowerings and the strengths.

(2) That the experimental errors did not appear in their true relations to the lowerings.

(3) That the experimental error was not multiplied to the same extent at different strengths.

Mr. Jones's numerical illustrations, however, had clearly shown that in both (1) and (2) the word lowering was made to bear two different meanings—the actual lowering (D), and the ($D - xm$) of the modified plotting; and in (3) the words "experimental error" did *not* mean the experimental temperature error (which would necessarily be represented on a constant scale for all strengths in the modified diagram), but a ratio which turned out to be simply $D - xm : D$, *i.e.*, the ratio of the ordinates of an ordinary and modified plotting drawn to the same scale. The numerical results obtained by Mr. Jones were simply a mathematical consequence of the fact than in the imaginary case he took, the actual lowerings were not exactly proportional to the strengths, and the only legitimate conclusion to be drawn from them (except the obvious one that the two forms of plotting were not identical) was that the modified plotting was perfectly adapted to the use to which it had been put by Mr. Pickering, viz., to render slight irregularities, which could otherwise be only adequately revealed by a troublesome mathematical investigation, at once obvious to the unaided eye.

*13. "*The Conditions in which Carbon exists in Steel.*" By J. O. Arnold and A. A. Read.

The authors have carried out experiments on the condition in which carbon exists in normal, annealed, and hardened steels on a series of five steels containing 0·96, 0·57, 0·33, 0·16, and 0·06 per cent of carbon respectively.

The method they have used in their determinations is a modification of the process of Binks and Weyl, originally proposed for the estimation of carbon in iron.

Two bars of polished steel of suitable size were suspended in separate beakers containing dilute hydrochloric acid (rel. dens. 1·02), placed in the same circuit, and connected with the positive pole of a single Bunsen cell, the cathodes being plates of platinum placed in a flat porous cell. At the end of the time allowed for solution, the carbide was collected on a smooth filter-paper and washed with water, alcohol, and finally with ether. The residue was washed off the filter paper into a weighed boat, and then dried in a vacuum. The carbon was estimated by direct combustion, the residue afterwards being used for the estimation of the iron.

From the results of a number of experiments the authors draw the following conclusions:—

1. The existence is confirmed of a carbide of iron possessing the formula Fe_3C, originally discovered by Abel and Müller by independent methods.

2. The normal carbide exists in two different forms identical in chemical composition.

(*a*) A diffused carbide is scattered in granules or very small plates throughout the iron in normal steel. When isolated it is a greyish black powder.

(*b*) A crystalline carbide, arranged in comparatively large distinct plates in well-annealed steel; these plates are chiefly in the form of well-marked striæ, and consist of pure Fe_3C. They are identical with the microscopical laminæ of Sorby's "pearly" constituent, and they may be isolated as bright silver plates.

3. The percentage of the total carbon obtained as carbide is greater in hard than in soft steels.

In iron containing ..	0·1	p. c.;	92	p. c.	Loss	8	p. c.
" " ..	0·5	" ;	87	"	"	13	"
" " ..	0·25	" ;	74	"	"	26	"

4. The above-mentioned loss does not appear to be due to decomposition, but rather to the presence of a readily decomposed subcarbide of iron (containing less carbon than the normal compound) existing to the extent of about 25 per cent in mild steel, and capable of existing to the same amount in cold hard steel after the latter has been heated for some time at a white heat.

5. The loss being practically the same in well-annealed steel as in the normal steel, it cannot be due, as supposed by Ledebur, to the presence of "hardening carbon."

6. The carbon in hardened steel exists chiefly as an extremely attenuated carbide, or in solution, leaving on isolation a residue consisting mainly of "hydrate of carbon," mixed to a slight extent with carbide of iron. Whether the large loss of carbon (about 50 per cent of the total) occurring during the galvanic decomposition of the hardened steel is due to the presence of a large percentage of sub-carbide or to evolved hydrocarbons, formed by the action of nascent hydrogen on the finely-divided free carbon, there is no conclusive evidence to show.

The authors have also experimented on a steel containing 1·73 per cent of manganese and 0·55 per cent of carbon, and find that a portion of the iron is replaced by manganese, the double carbide apparently having the formula Fe_7MnC_3.

Discussion.

Professor Roberts-Austen observed that this was only a portion of a long series of experiments, many of which appeared to have been very carefully made. He regretted, however, to say that he entirely differed from the conclusions at which Mr. Arnold had arrived. He was not prepared to raise objections to the method employed, which, under the circumstances, was probably as good as any that could have been adopted; it was, moreover, a method which the speaker had himself used thirty years ago. He quite believed in the existence of Abel's carbide of iron, Fe_3C, but he considered that the authors of the paper had not offered any evidence which could be accepted in support of the presence in the steel of a new sub-carbide of iron. Without the exercise of the utmost care and absolute uniformity of conditions, nothing is easier than to lose carbon when steel is dissolved by electrolytic action.

Mr. Bertram Blount said that he had had some experience in the use of the method described by the authors for isolating the carbon in steel, and had observed that the conditions of experiment had to be arranged in such a manner as to confine the reaction between certain limits. On the one hand, an insufficiency of current permitted the escape of hydrogen (and therefore of hydrocarbons) due to the action of the acid on the iron *per se*; and on the other an excess of current might exert so strong an oxidising influence as not only to determine the complete suppression of the hydrogen and oxidation of ferrous to ferric chloride, but also to attack the carbon or carbides, the isolation of which was sought. It followed that the range for safe working lay between the point at which all the iron was converted into ferrous chloride without evolution of hydrogen as a lower limit, and that at which all the ferrous chloride was converted into ferric chloride, as an upper limit. In conclusion, he would

plead for a more general observance of the necessity of stating the precise working conditions, *e.g.*, voltage and current density, in describing electrolytic experiments, in order that any given experiment might be repeated at any time under conditions identical with those adopted by a previous observer.

14. "*The 'Cis-' and 'Trans-' Modification of Tetramethylenedicarboxylic Acid* (1.2) *and Pentamethylenedicarboxylic Acid* (1.2)." By W. H. Perkin, jun., F.R.S.

The author has further investigated the tetramethylenedicarboxylic acid (1-2) which had been previously obtained (*Trans.*, li., 23) by heating the disodium derivative of ethylic butanetetracarboxylate,—

$$(COOC_2H_5)_2{\cdot}CNa{\cdot}CH_2{\cdot}CH_2{\cdot}CNa(COOC_2H_5)_2,$$

with bromine, hydrolysis of the product, and elimination of two molecules of carbon dioxide at 200°.

The acid (m. p. 138°) thus obtained is the *cis*-modification, since when digested with acetyl chloride it yields an anhydride, $C_6H_6O_3$ (m. p. 75°), which dissolves in water, regenerating the same acid.

The *trans*-modification of tetramethylenedicarboxylic acid is obtained by heating the *cis*-acid with hydrochloric acid at 180°; it melts at 130°, and does not yield an anhydride when digested with acetyl chloride; on distillation, however, it is partially converted into the anhydride of the *cis*-acid.

Pentamethylenedicarboxylic acid (1-2) is obtained by an exactly similar series of reactions from ethylic pentanetetracarboxylate (*Trans.*, li., 244), but the acid (m. p. 160°) produced in this case is the *trans*-modification.

This, when heated with acetyl chloride at 140°, is decomposed, forming the anhydride of the *cis*-acid (m. p. 73°). *Cis*-pentamethylenedicarboxylic acid is obtained from this anhydride by dissolving it in potash; it melts at 140°, and is much more readily soluble in water than the *trans*-acid into which it is quantitatively converted by heating with hydrochloric acid at 180°.

Baeyer, in his remarkable paper on the hexahydrophthalic acids (*Annalen*, cclviii., 145) expresses the opinion that *trans*-pentamethylenedicarboxylic acid, like *trans*-hexahydrophthalic acid, should yield an anhydride of its own; but so far the author has not been successful in preparing this substance.

15. "*Hexamethylenedibromide*,—

$$Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br."$$

By E. Haworth and W. H. Perkin, jun., F.R.S.

This substance may be obtained by the following series of reaction:—

Chloromethoxypropane, $Cl(CH_2)_3OCH_3$, is first prepared by heating chlorobromopropane, $Cl(CH_2)_3Br$, with sodium methoxide. It is a colourless oil, which boils at 119°, and when acted on in benzene solution with potassium, is converted into a high boiling oil which apparently contains dimethoxyhexane, thus—

$$2Cl{\cdot}(CH_2)_3OCH_3 + K_2 = CH_3O{\cdot}(CH_2)_6OCH_3 + 2KCl.$$

From this substance hexamethylene dibromide is obtained by the action of fuming aqueous hydrobromic acid at 150°. It is a colourless oil, which boils at 137—140° (20 m.m.).

When a solution of this dibromide in *m*-xylene is acted on with sodium, a hydrocarbon, C_6H_{12}, is produced which boils at 77—80°, and is apparently identical with hexamethylene, which Baeyer (*Annalen*, cclxxviii., 111) obtained in the course of his researches on the reduction of benzene.

Hexamethylenedibromide reacts readily with the sodium derivative of ethylic malonate, sodium bromide being separated, and an oily product formed, which, when fractionated under reduced pressure, is separated into two fractions, boiling at 130—220° and 220—290°.

The lower fraction, on hydrolysis, yields an oily acid, from which, on distillation, a small quantity of substance was isolated, which boiled at 248—250°, and on analysis gave numbers agreeing with the formula $C_8H_{14}O_2$. This substance appears to be heptamethylenecarboxylic acid.

The higher fraction contains ethylic octanetetracarboxylate,—

$$(COOC_2H_5)_2{\cdot}CH{\cdot}(CH_2)_6{\cdot}CH(COOC_2H_5)_2,$$

a colourless oil, which boils at 275—280° (60 m.m.); on hydrolysis it is converted into a polybasic syrupy acid, which at 200° rapidly loses carbon dioxide forming sebacic acid, $COOH(CH_2)_8COOH$.

16. "*α-Hydrindone and its Derivatives.*" By F. Stanley Kipping, Ph.D.

The author gives an account of the preparation of α-hydrindone by the action of aluminium chloride on phenylpropionic chloride (*Proc. Chem. Soc.*, cxvii., 216), and points out that this method is very convenient for the preparation of large quantities of this ketone. When suitable conditions are chosen, the yield is very good, and, with the exception of one by-product, namely, a substance which probably has the constitution—

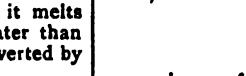
$$C_9H_7O{\cdot}CCl{:}CH{\cdot}CHPh,$$

no other compound is formed.

After referring to the behaviour of hydrindonoxime under various conditions, and bringing forward conclusive evidence that the oxime is converted into hydrocarbostyril by the action of phosphorus pentachloride (*Proc. Chem. Soc.*, cxxix., 240), several derivatives of hydrindone are described; amongst others, the products of condensation with benzaldehyd and with acetone, and a compound of the composition $C_{18}H_{14}O$, formed by condensation of two molecules of the ketone—

$$2C_9H_8O - H_2O = C_{18}H_{14}O.$$

This substance is considered to be anhydrobishydrindone,—



an analogue of the anhydrobisdiketohydrindene, prepared by W. Wislicenus and his co-workers. As, however, some of its properties do not completely harmonise with this view of its constitution, the investigation is being continued.

NOTICES OF BOOKS.

Practical Paper-Making: a Manual for Paper-makers, and Owners and Managers of Paper Mills. By George Clapperton. London: Crosby Lockwood and Son. 1894.

The art of paper-making has of late years made such rapid strides, owing to the enormous increase of all classes of literature—many hundreds of miles of paper being now used every night for newspapers in London alone—that to meet this increase new raw materials have been pressed into the service of the paper-maker.

In the volume now before us, the author has briefly but clearly described all the various processes now in vogue for making paper from the different substances now in use, and he trusts that this volume will supply a want he has himself felt for years—more especially during his apprenticeship—viz., a work which combines the necessary theoretical teaching with a due consideration of the practical side of the question. Taking the book *seriatim*—

Chapter I. deals with the chemical and physical characteristics necessary in fibres to render them serviceable in the manufacture of paper.

The next two chapters give in detail the processes of cutting, boiling, picking, bleaching, &c., of rags and jute. We then come to the now important subject of cellulose from wood, and mechanical wood pulp. Comparatively few paper-makers in this country prepare their own wood pulp, the bulk of it coming from Sweden and Norway,

although some of the best is turned out in Scotland. The processes employed to break up the combination of the two parts of cellulose with one part of non-cellulose which go to form wood, may be classed under three heads, viz., the caustic soda or alkali process; the acid process, comprising the various methods of employing liquid or gaseous sulphurous acid; and, midway between these two, the sulphate process. Whichever of these be used, the wood must first be prepared mechanically, the methods used for doing this being here fully given. Esparto and straw undergo treatment not dissimilar to that undergone by wood; the differences of detail in working being shown in Chapter V. The relative merits and demerits of long and short fibres are next discussed; while the seventh to the twelfth chapters complete the round of operations by describing *in extenso* the several processes of loading, colouring, and sizing, glazing, finishing, &c. The author here pleads that in adding "loading" materials to the paper, the paper-maker is not acting in a manner akin to the dishonest milkman, as is commonly believed, but he shows that the loading is added with the distinct view to making the paper more suitable for the particular purpose to which it is to be applied. "In the case of printing-papers especially," he says, "the addition of 15 or 16 per cent of loading, by making them more absorbent, enables them to print much better, and lessens in a considerable degree the friction when in contact with the types."

In a chapter on the microscopical examination of paper, he expresses the opinion that the reagents commonly in use for this purpose are of very little real service, inasmuch as the fibres most easily distinguished by their means are precisely those which are the most easily recognised without their use. He, however, goes fully into the practice of this examination, and gives a number of excellent plates showing papers made from various fibres, magnified 130 times.

The remaining chapters are devoted to tests for ingredients in papers, the recovery of soda and other chemical matters, concluding with a useful appendix giving tables and data specially adapted for paper-making.

The book being intended for the use of practical men, will account for the free use of technical terms, but ordinary readers will be naturally somewhat mystified by such words as "potcher," "deckle," "dandy," &c.

Mr. Clapperton has evidently a thorough knowledge of his subject, and we have no doubt but that this volume will be widely appreciated by all connected with this important and ever-growing industry.

The Dentists' Register. Printed and Published under the Direction of the General Council of Medical Education and Registration of the United Kingdom. London: Spottiswoode and Co. 1894.

THERE have been probably more "quacks" in dentistry than in any other branch of medical science, and the general public have necessarily suffered therefrom. The act passed in 1878 put a salutary check on those gentry calling themselves dentists, who used to extract teeth (and not always the bad ones) to the sound of drums and trumpets, by obliging all dental practitioners to be officially registered, under a penality not exceeding twenty pounds.

It is important for registered dentists to know that after the publication of their names in *this* register, that alone is the legal evidence of registration. This volume therefore serves the double purpose of an "Official List" and a "Directory."

There are, we find, nearly 5000 dentists in the United Kingdom, of whom nearly 3500 have no additional qualifications beyond that of the dental colleges, the balance being either surgeons or physicians as well.

The Dental Registration Fund is evidently in a prosperous condition, there being, at the end of December, 1893, a balance in hand of over £7500.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 19, May 7, 1894.

Spectra of Oxygen at High Temperatures.—J. Janssen.—Already inserted.

Gases Isomeric with Propylene and their Sulphates. — M. Berthelot. — There are two substances corresponding to the formula C_3H_6 which represent the simplest case of isomerism known among gaseous bodies. One of them is ordinary propylene, which furnishes the isopropylic ethers and alcohol. The other is trimethylene, which yields normal propylic ethers and alcohol. According to the determinations of the heat of combustion, ordinary propylene should be the true homologue of ethylene, being formed by the addition of carbon and hydrogen, with a normal liberation of +5·2 cal., whilst trimethylene would be formed by setting out from ethylene with absorption of −2·5 cal. It contains therefore with reference to propylene an excess of energy amounting to +7·7 cal., an excess which seems incompatible with the cyclical constitution ascribed to trimethylene.

Proposed Monument to the Memory of Lavoisier.—The Perpetual Secretary read a communication from G. Hinrichs, who suggests that the chemists of all nations should erect a monument in honour of Lavoisier. M. Grimaux presented an analogous proposal. The Academy decided that the question should be referred to the examination of the Administrative Commission.

Absorption-spectra of Cupric Bromide. — Paul Sabatier.—This paper will be inserted in full.

Variations of Viscosity in Melted Sulphur.— J. Brunhes and J. Dussy.—The speed of flow of melted sulphur increases from the point of fusion to a temperature between 156° and 157°. Above that limit it decreases rapidly and becomes so viscid that at 162° it no longer flows in tubes of 1 m.m. in diameter under a pressure measured by a column of mercury of 700 m.m. The flow of sulphur at 156° is equal to $\frac{1}{1000}$ of that which it has at 115·5°.

Blue Lakes Derived from Dibromogallanilide, and certain Blue Reactions of the Polyphenols. — P. Cazeneuve.—If we carefully add ammonia or a solution of potassa or soda to a solution of dibromogallanilide, we obtain a substance of an indigo-blue colour, easily modified by an excess of air or of base. The colour turns to green and then to yellow. The zinc lake is more stable. A fact worthy of attention is that all the polyphenols derived from pyrogallol yield blue compounds.

Aldehyd of Oil of Lemon-grass.—This paper does not admit of useful abstraction.

Industrial Manufacture of Products Rich in Nicotine.—Th. Schlœsing, jun.—Extracts of tobacco can be successfully applied for combating epidemic parasites both on plants and animals. In the La Plata country liquids are used containing at most 200 grms. nicotine per litre. This liquid for application to animals is diluted with 80 vols. of water. For plants solutions of nicotine at $\frac{1}{10000}$ are very suitable.

Oxidation of Worts of Beer.—P. Petit.—In the employment of apparatus for the introduction of air, the current must be so regulated as not to carry off all the aroma. Wort appears to consume 570 c.c. of oxygen per hectolitre for chemical reactions.

Researches on the Chemical Transformations of the Fundamental Substance of Cartilage during Normal Ossification.—C. Chabrié.—The author regards the totality of the reactions in the transformation as consisting of (1) the substitution of NH_2 for OH; (2) the disappearance of a sulphur compound or the substitution of NH_2 for SO_2OH; (3) an oxidation; (4) probably a condensation.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Aluminium—Chlorate of Potash.—I have read that "a French syndicate has recently been formed for establishing factories of aluminium and chlorate of potash and for electro-metallurgical appliances, near Martighy in Switzerland," to be operated by water power. Also, that "an immense water-power plant is being erected in Sweden for the electrical production of chlorate of potash." Will you kindly tell me if either of these industries is in operation?—INTERESTED.

MEETINGS FOR THE WEEK.

TUESDAY, 29th.—Royal Institution, 3. "The Modern Microscope: an Instrument for Recreation and Research," by the Rev. W. H. Dallinger, F.R.S.
—— Society of Arts, 8. "Black and White in Afrikanderland," by W. A. Wills.
—— Institute of Civil Engineers, 8. (Anniversary).
WEDNESDAY, 30th.—British Astronomical, 5.
THURSDAY, 31st.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "Egyptian Decorative Art," by Prof. W. M. Flinders Petrie, D.C.L.
FRIDAY, June 1st.—Royal Institution, 9. "The Work of Herts," by Prof. Oliver Lodge, D.Sc., F.R.S.
—— Geologists' Association, 8.
—— Quekett Club, 8.
SATURDAY, 2nd.—Royal Institution, 3. "The Stage and Society," by Robert W. Lowe.

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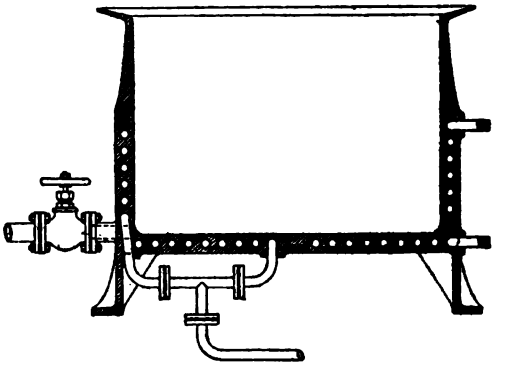

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says:—

P. 316. "An improved vessel for boiling oil, and suitable for many other kindred purposes, has been recently described by T. Frederking (CHEMICAL NEWS, London). A coil of stout piping is arranged in a casting mould, so that the molten metal forming the pan is cast round the coil, much as is done in the case of the water-tuyeres of a blast furnace. Steam at any pressure [or any other heating medium] being passed through the coil, the pan is heated up proportionately without any danger, the pressure bearing solely on the piping and not on the metal pan itself, whilst the well conducting metal walls allow the heat to pass readily. Temperatures up to 350° and 400° C. can be thus obtained."

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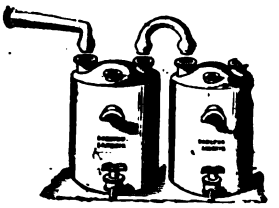

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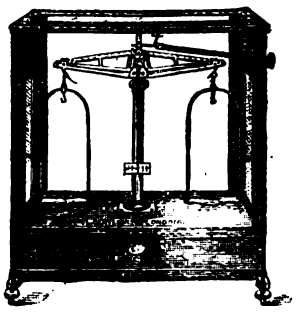

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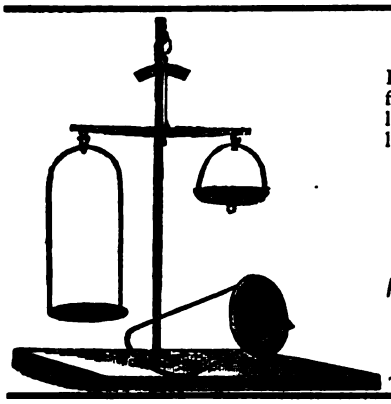

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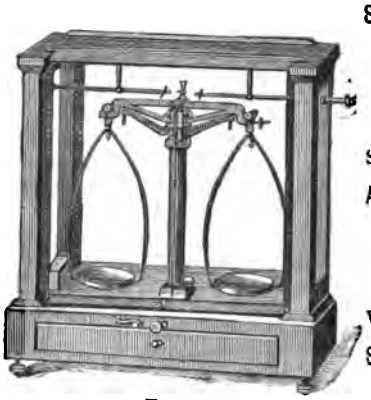

FIG. 3a.

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THE CHEMICAL NEWS.

Vol. LXIX., No. 1801.

THE ANNUAL GENERAL MEETING OF THE CHEMICAL SOCIETY.

The Address delivered by the President, Dr. Armstrong, F.R.S., must be considered as of the utmost importance, and may justly claim the heedful attention of every chemist, even though he may not agree with all the views of the speaker.

The first point of general interest is the value to be set upon the letters F.C.S. If we understand Dr. Armstrong aright, he would adopt "a policy of absolute free trade." That is, we suppose, that every person paying the fees might be at once invested with the Fellowship of the Society. Whether this step would not greatly impair the value of the Fellowship and render it less coveted is at least a very open question.

"Science and Art Department teachers," complains Dr. Armstrong, "have been largely under a ban." Such ban is not unjustifiable if we consider how largely examinational has been their training.

The imperfect chemical attainments of medical men are very justly regretted. We cordially agree with the suggestion that "they should be taught the principles of scientific method instead of being allowed to crowd their memories with mere facts," which, if wanted, could at any time be found in a text-book.

Much more to the purpose is Dr. Armstrong's complaint of the increased, and still increasing, bulk of chemical literature. The number of journals grows, and besides those referred to in the Presidential Address, there are others published in Britain into which facts of chemical importance may find their way. As to valuable matter in other languages the case is still worse. Important researches may appear veiled in Russian, Polish, Czech, Servian, and Roumanian garb. We should like to see the suggestion of a German writer adopted, viz., that whatever is not given to the world in German, English, or French should not be treated as published.

The needless prolixity of many chemists and their indulgence in incorrect language are not overlooked. American and German students are here not free from blame.

Dr. Armstrong's expressed regret "that the brilliant workers we can count among Englishmen are mere sporadic excrescences on a general dead level of mediocrity," would be needless were it not for the examinational education to which we still cling.

The Burlington House societies, we are told, find themselves oppressed or about to be oppressed by insufficient space. But when Dr. Armstrong hopes that the Artists may find more suitable quarters elsewhere, he does not consider that a little aimless gossip on this subject was vented in the House of Commons a few days ago, when it appeared that the Academy holds a lease of which more than nine centuries are unexpired.

We are happy to find Dr. Armstrong hoping that the Institute of Chemistry "will allow the utmost latitude in matters educational," and deprecating "any attempt to claim exclusive privileges for the Fellows."

The Goldsmith's Company must be congratulated on its wise liberality in granting £1000 to the Imperial Institute "to defray the cost of fitting up and equipping the Research Department." Perhaps this and similar facts will not be entirely ignored by those persons who are eager to confiscate the possessions of the City Companies.

An improvement in the appointment of inspectors under the Art and Science Department is announced. We submit that so long as "results" are understood to mean the number of pupils who "pass" this or that examination, the system can be mended only by being ended.

Dr. Armstrong's strictures on the examination system and its sad effects are above all praise. We cannot select for commendation any particular passages from the section headed "Progress in Education." But we note that he looks to the new Royal Commission on Secondary Education to recommend drastic changes. We hope that none of our friends will omit to read, mark, learn, and inwardly digest this portion of the Presidential Address.

We will merely remind our readers that our most formidable rival, Germany, has no Boards of Examiners, no standards, no books written for students preparing for one or other examination, but that she awards honours according to *rebus gestis*.

NOTES ON THE CUPELLATION OF BISMUTH-SILVER ALLOYS.*

By ERNEST A. SMITH, Assoc. R.S.M.,
Assistant Instructor in Assaying, Royal School of Mines, London.

The loss of silver by the cupellation of lead-silver alloys has been the subject of a large number of experiments at various times, but comparatively few results have been published on the loss of silver by the cupellation of bismuth-silver alloys.

A series of experiments were made some years ago by Mr. Hambley† on the cupellation of lead-silver alloys, which prove that according to the decrease of weight of the silver cupelled, so the loss of that metal very slightly increases, provided the ratio of lead employed be constant. His results also confirm the fact that an increasing ratio of lead produces an increasing loss of silver.

The following experiments were made to ascertain whether the loss of silver by cupellation was the same when varying quantities were employed with a constant ratio of bismuth in the place of lead, and also to find the loss of silver when cupelled with a gradually increasing ratio of bismuth. The quantities of bismuth and silver taken were the same as those employed by Mr. Hambley for the experiments with lead and silver given in Tables I. and III.

The bismuth and the silver employed were specially purified before use.

The temperature employed was slightly lower than that usually employed for the cupellation of lead-silver alloys, the melting-point of bismuth (270° C.) being somewhat below that of lead (334° C.).

The results obtained are given in the following Tables:—

Table I.

Mean Results of Cupellation Obtained by Mr. Hambley with Constant Ratio of Lead and Silver.

Quantity of lead employed. Grains.	Quantity of silver employed. Grains.	Mean weight of silver obtained. Grains.	Calculated weight of silver p. c.	Loss of silver per cent.
250	25	24·733	98·932	1·068
100	10	9·886	98·865	1·135
10	1	0·988	98·775	1·225

Table II.

Mean Results Obtained by the Author with a Constant Ratio of Bismuth and Silver.

250	25	24·391	97·566	2·434
100	10	9·741	97·416	2·584
10	1	0·973	97·370	2·630

* Abstract of a Paper read before the Chemical Society, May 17, 1894.

† *Chem. Gaz.*, 1856, pp. 185–6.

Mr. Hambley has concluded that, provided a constant ratio of lead and silver be employed, the loss of silver very slightly increases according to the decrease in the weight of the silver cupelled.

From the above results the conclusion may be drawn that a very much greater loss takes place when bismuth is present instead of lead under the same conditions, although the ratio of the loss appears to be about the same.

In the following Tables 5 grains of silver were used in each case. Table III. gives the mean results obtained by Mr. Hambley with lead and silver, and Table IV. those obtained by the author with bismuth and silver.

TABLE III.

Lead employed. Grains.	Ratio of lead and silver.	Percentage of silver.	Weight of silver obtained. Grains.	Calculated loss of silver per cent.
5	1 to 1	50·00	4·972	0·55
15	3 „ 1	25·00	4·955	0·90
25	5 „ 1	16·16	4·945	1·11
35	7 „ 1	12·50	4·941	1·18
45	9 „ 1	10·00	4·933	1·34
50	10 „ 1	9·09	4·924	1·52
75	15 „ 1	6·25	4·919	1·62
100	20 „ 1	4·76	4·916	1·68
125	25 „ 1	3·84	4·912	1·76
175	35 „ 1	2·77	4·906	1·88

TABLE IV.

5	1 to 1	50·00	4·967	0·660
10	2 „ 1	33·33	4·964	0·720
15	3 „ 1	25·00	4·955	0·900
25	5 „ 1	16·16	4·940	1·190
35	7 „ 1	12·50	4·924	1·520
45	9 „ 1	10·00	4·909	1·820
50	10 „ 1	9·09	4·898	2·034
75	15 „ 1	6·25	4·878	2·428
100	20 „ 1	4·76	4·832	3·354
125	25 „ 1	3·84	4·808	3·840
175	35 „ 1	2·77	4·768	4·640

The results given in Tables III. and IV. tend to confirm the fact that an increasing ratio of lead or bismuth produces an increasing loss of silver, the loss, however, being much greater in the case of bismuth.

To determine with accuracy and in a thoroughly satisfactory manner the extent and exact ratio of the loss of silver experienced in the cupellation with either lead or bismuth, a much larger number of cupellations are requisite.

As the loss of silver by volatilisation during cupellation is altogether inconsiderable unless the temperatures at which the operation has been conducted has been much too high, the source of loss is evidently due to the fact that the silver is absorbed by the cupel.

The following result was obtained by the cupellation of the lead extracted from a cupel upon which 175 grains of lead with 5 grains of silver had been cupelled.

	Grains.	P. c.
Weight of silver button from 1st cupel..	4·908	= 98·16
„ „ „ 2nd „ ..	0·075	= 1·50
Total silver	4·983	= 99·66
Loss..	0·017	= 0·34
	5·000	= 100·00

The cupellation of the bismuth extracted from a cupel used for the cupellation of 175 grains of bismuth with 5 grains of silver gave—

	Grains.	P.c.
Weight of silver button from 1st cupel..	4·795	= 95·90
„ „ „ 2nd „ ..	0·204	= 4·08
Total silver	4·999	= 99·98
Loss..	0·001	= 0·02
	5·000	= 100·00

The results of the experiments given tend to show the importance of using "checks" when making bullion assays containing bismuth.

"A NEW ELEMENT?"

By Dr. K. J. BAYER.

THE *Chemiker Zeitung* publishes under this title the following interesting communication:—

On a thorough examination of that portion of the French beauxite which after ignition with soda or potash is soluble in water, I obtained, after separating the dissolved aluminium, vanadium, and chromium, as also the greatest part of the salts which could be crystallised out, a substance showing reactions which cannot be harmonised with those of any of the known elements. The characteristic compounds of this substance seem to be those in which it acts as a metallic acid.

The acid itself is a yellowish brown infusible substance which dissolves in water with an intense golden yellow colour, and forms salts either of a rather paler colour or of a hue varying from dark olive green to brown. In the solutions of the ammonium salt, strong ammonia produces a dark green precipitate of the ammonium salt, which, on heating, re-dissolves in water with a dark olive-green colour. In such solutions we obtain the following reactions:—

Barium chloride gives a yellowish green precipitate, which easily dissolves in acids with a yellow colour.

Mercurous oxide solutions likewise give a pale straw-coloured precipitate, soluble in nitric acid, and which, on evaporation, forms small wart-shaped crystals.

Silver nitrate gives a greenish precipitate, soluble both in ammonia and in nitric acid. The silver salt crystallises out from the ammoniacal solution.

Magnesia mixture gives at first nothing, but on standing there falls a green crystalline precipitate, as in the case of phosphoric acid, especially where the sides of the vessel have been rubbed. If deposited slowly, the precipitate forms transparent crystals, of an olive-brown colour, capable of being distinguished with a lens. This precipitate also readily dissolves in acids, with a yellow colour.

The separation with magnesia mixture is tolerably complete, and the liquid, which is at first greenish, becomes ultimately colourless. Still, barium chloride produces in it a slight greenish precipitation.

Molybdenum liquid gives in solutions acidulated with nitric acid a whitish precipitate on heating. The precipitate subsides with difficulty, but the precipitation is very incomplete, and the supernatant liquid has still a decided yellow colour.

Sulphuretted hydrogen on introduction into the alkaline liquid converts it into the corresponding sulpho-salt of an intense red colour. In this solution acids precipitate a rusty brown sulphide. This precipitation is also incomplete, and the supernatant liquid retains a violet colour from a lower stage of oxidation in solution. In acid solutions H_2S gives no precipitate, but reduces the originally yellow solution to a violet liquid, holding a lower oxide in solution. If this solution is evaporated down in an open vessel, it absorbs oxygen after the escape of the hydrogen sulphide and becomes yellow again. If the violet solution is evaporated with exclusion of air, it gives with am-

monia a voluminous precipitate of an intense violet colour, which soon becomes crystalline, but the supernatant liquid retains its violet colour. Soda and sodium carbonate also effect a partial precipitation, but the precipitate readily re-dissolves in an excess of the precipitant.

Hydrogen peroxide does not occasion any change of colour or precipitation either in alkaline or acid solutions. (A point of distinction from vanadium).

Potassium ferrocyanide, a very sensitive reagent for vanadium and for molybdenum in acid solutions, gives in the acid solutions of this substance neither a precipitate nor a change of colour. A solution which had been supersaturated with ammonium chloride for the removal of the vanadium might, I hoped, have been freed from this substance by ignition. Unfortunately I experienced a considerable loss of the substance in question, which volatilised as a chloride along with the vapours of ammonium chloride, forming a yellow sublimate, soluble in water. The escaping fumes, which came in contact with the flame-gases between the porcelain crucible and its lid, were decomposed by the water-vapour, so that a violet-brown non-volatile coating was deposited on the crucible and its lid, evidently representing the oxide corresponding to the violet solution, whilst hydrochloric acid was driven off. When I subsequently heated the violet-brown coating with access of air, it gradually assumed a pale yellow colour and was re-converted into the metallic acid.

Unfortunately I have failed in obtaining sufficient material for preparing some characteristic compounds and determining the atomic weight. Still, I believe I am warranted by the reactions above mentioned in suspecting the presence of a new element concerning which I hope in time to make further communications.

ABSORPTION-SPECTRA OF CUPRIC BROMIDE.

By PAUL SABATIER.

In a former communication I have mentioned the variety of colours displayed by solutions of cupric bromide, and the extraordinary opacity presented by some among them.

For the examination of the spectra I have used Crova's spectro-photometer. The two sources of light were two Auer incandescent burners, joined to one and the same gas-pipe with the interposition of a pressure regulator, and each fitted with a metal chimney, and each having a small perforation for the passage of the light.

The solutions examined were placed in perpendicular troughs with surfaces perfectly parallel and of exactly known thicknesses. To eliminate the influence of the inevitable inequality of the two lights and of the special absorption exerted by the sides of the troughs and by the reflections on their surfaces, I have proceeded as follows:—

On the track of the direct light between the trough for the liquids and the slit of the spectro-photometer we arrange the cats'-eye lens of Cornu's spectro-photometer, which gives on the slit a luminous image of the light and enables us by means of the cats'-eye to diminish its intensity at will.

The trough having been filled with the colourless solvent and the lateral Nicol being at zero, we gradually close the cats'-eye so that the direct spectrum has a brightness slightly less than the lateral spectrum. We then determine for the different radiations the ratio of the direct light $I\lambda$, which arrives at the slit to the stronger lateral light $\phi\lambda$. We find—

$$I\lambda = \phi\lambda \cos^2 w = K\phi.$$

We then substitute in the trough for the solvent the coloured liquid to be examined, whence there results a more or less energetic absorption. $I\lambda$ is reduced to $I'\lambda$, which is valued $I'\lambda = \phi\lambda \cos^2 w' = K'\phi$, whence we deduce—

$$\frac{I'\lambda}{I\lambda} = \frac{K'}{K} = \frac{m}{100},$$

m being the proportion (for 100) of the light transmitted.

Now the general law established for the transmission of a simple ray through the thickness e of an absorbent medium is expressed by the relation $I'\lambda = I\alpha^e$, α being a fraction which is named the coefficient of transmission.

On account of the magnitude of the absorbent power of certain solutions of cupric bromide, I have selected as normal liquid that containing per litre $\frac{1}{100}$ atom of copper, that is, 0·634 grm., e being expressed in c.m.

For such liquids we have—

$$\frac{m}{100} = \alpha^e, \text{ whence } \log.\ \alpha = \frac{\log.\ m - 2}{e}.$$

In solutions of different concentrations, but where the colouring matter exists in identical chemical conditions, the absorption depends only on the chemical mass placed in the track of the light. For a liquid in which $\frac{Cu}{100}$ occupies n litres, the thickness e will absorb litre $\frac{e}{n}$ of the normal liquid. The formula applied to such a liquid becomes—

$$\log.\ \alpha = \frac{n\ (\log.\ m - 2)}{e},$$

m being the centesimal proportion of the light transmitted, e the thickness in c.m. of the coloured solution, n the number of litres occupied by 0·634 grm. of copper in this solution.

For one and the same liquid we may cause e to vary at pleasure: it will be convenient to observe great thicknesses if the absorption is slight, but small thicknesses if the liquid is very opaque. The values of α relative to the different radiations as thus obtained for a given thickness may be represented by regular curves, the λ being taken as the abscissæ. The curves corresponding to the different thicknesses coincide and agree in a satisfactory manner, which yields a physical verification of the law of thickness.

The following are the chief results:—

1. *Dilute Aqueous Solution of Cupric Bromide* (*e.g.*, $CuBr_2 = 8$ litres).—The liquid has the ordinary blue colour of cupric salts. The absorption, well marked in the red, decreases rapidly and becomes very slight beyond the green.

A rise of temperature modifies these values by augmenting the absorption of the short radiations. The blue solutions turn green and approximate to the liquids examined below.

2. *Aqueous Solution more concentrated* (275 grms. bromide per litre or $CuBr_2 = 0{\cdot}81$ litre).—Here the absorption is energetic in the red and has a well-marked minimum in the green $\lambda = 555\ \mu\mu$; it then increases rapidly towards the blue and the indigo. There results a dark green tint identical with that of the crystals $CuBr_2.4H_2O$. If these green solutions are heated they become brown.

3. *Very concentrated solutions, e.g.*, from 600 to 1000 grms. anhydrous bromide per litre. These solutions present an extreme opacity, which does not allow their absorption-spectra to be measured, except in very shallow layers, below 1 m.m., and, consequently, difficult to determine with precision. This circumstance does not enable us to measure the coefficient α with a sufficient accuracy. We may, however, ascertain that the transmission has its maximum in the red, bordering on the orange, $\lambda = 640\ \mu\mu$, when the absorption increases rapidly towards the green. The result is a brown tint, yellowish red in slender layers.

4. *Solutions of Anhydrous Cupric Bromide in Absolute Alcohol.*—Here the absorption-spectra are alike at all

concentrations, and seem similar to those of very concentrated aqueous solutions. The maximum transmission is at λ 640 μμ. We may hence conclude that highly concentrated aqueous solutions contain the salt to a great extent in an anhydrous state.

The absorption becomes still more intense in hydrobromic solutions, which we shall examine in a future paper.—*Comptes Rendus*, cxviii., p. 1042.

SEPARATIONS OF METALS.*

New Quantitative Separations of the Metals of the Sulphuretted Hydrogen Group in a Current of Bromine Vapour or of Chlorine.

By P. JANNASCH and P. ETZ.

(Concluded from p. 235).

The expulsion of bismuth by bromine is best effected when a rather plentiful quantity of sulphur has accompanied the sulphuretted hydrogen precipitate. It may be advantageous before the introduction of the sulphuretted hydrogen to add to the hydrochloric solution of the metals a few drops of red fuming nitric acid.

Before introducing the porcelain boat charged with the mixed sulphides into the tube of potash glass, effect a sufficient comminution and a uniform distribution of the substances by means of a platinum rod so as to effect a thorough and rapid action of the bromine and to prevent the mass from spirting, which readily happens if large fragments are present.

Further, the current of bromine vapour must be made very rapid from the beginning of the operation (about 300 gas bubbles per minute from a glass tube of the width of 6 m.m.), as a certain lack of bromine evidently interferes with the formation of the volatile bismuth tribromide. At the beginning a backwards sublimation must be carefully evaded. At the end of the bromation, and whilst the tube is cooling, the current of gas must be suitably moderated.

It has been found suitable not to heat the mixed sulphides too long to 100° in the drying closet, but to put an end to the desiccation when the loss of weight of the substance, which has been dried for some time, after further desiccation for about fifteen minutes, does not go beyond a few m.grms.

It is then, however, necessary before the commencement of bromation to heat the substance in the boat very gently in a current of dry air, and to drive any escaping water into the receiver. An excessive heat is to be avoided as expelling bismuth in a current of bromine. It is perfectly easy to distil over the bromide with a Bunsen flame of 8 c.m. in height. We proceed as follows:—The tube is first heated in front of the boat with a fanning flame in order to prevent back-sublimation, and we then proceed to the boat itself. Here we heat very gradually until the residual lead bromide melts (which is easily observed), and then we attend to the product of sublimation. When we have driven all the bismuth forwards as much as possible, we return with the flame to the boat, heat again to fusion, and observe if there appears a yellow coating on the tube. This will generally occur two or three times, but if nothing further passes over at the melting temperature of the lead bromide we do not heat more strongly, but allow the substance to cool quietly in the current of bromine. The procedure, as above described, takes up from forty-five to sixty minutes.

The lead is once weighed directly in the boat as bromide, and then finally as sulphate. It is converted into this last form by heating the bromide with saturated chlorine water and precipitating the solution of lead chloride thus obtained with sulphuric acid. Towards nitric acid the fused lead bromide thus obtained proved extremely resistant, so that it could not be obtained in solution. Bismuth could not be detected in the preparation.

The nitric-bismuth solution from the receivers, after suitable concentration, is precipitated with ammonium carbonate at a boiling heat, and the precipitate is weighed as bismuth oxide. The ignited oxide may be conveniently covered with a little solution of ammonium carbonate, evaporated on the water-bath, then heated more strongly in the air-bath, and finally ignited in order to expel slight traces of accompanying sulphuric acid. No lead could be detected in the weighed bismuth oxide.

According to the accompanying confirmatory analyses, the authors obtained satisfactory results both in the separation of bismuth and cadmium and in that of bismuth and lead. A practical application of this method of separation is found in the analysis of special alloys, such as Wood's metal. For this purpose, according to Jannasch and Etz, two different methods may be taken. The authors first proceeded as in the separations above described, and attempted then a direct conversion of the metals into sulphides by melting the alloy with sulphur in a current of carbon dioxide.

The alloy used was obtained by melting together bismuth, lead, tin, and cadmium about in the proportions 15 : 8 : 4 : 3, and a large pure portion, after the removal of the layer of oxide, was comminuted. About 1 grm. of the substance was dissolved in dilute aqua regia in a deep porcelain capsule, and the solution evaporated to dryness.

The chlorides formed are rinsed into a large beaker with water, and so much hydrochloric acid that at a boiling heat everything remains in a clear solution, and sulphuretted hydrogen is passed into the hot liquid. After about thirty minutes it is advisible to neutralise the free acid sufficiently, and then to proceed with the introduction of the sulphuretted hydrogen. After the precipitation is complete, filter through a weighed filter, dry the precipitate at 100°, introduce it into the bromation tube, and begin to heat with a movable flame. Then begins the distillation of sulphur bromide, tin and bismuth bromides, whilst the lead and cadmium bromides remain in the boat and gradually melt. As soon as this takes place the fanning movement of the flame is continued and everything which has sublimed into the glass tube is driven into the receivers. If a faint white coating (lead chloride) appears on the tube above the boat this is left behind without attempting to drive it away by a more intense heat, lest traces of lead and cadmium bromides might be volatilised.

* *Journal f. Prakt. Chemie* and *Berichte.*

METHODS OF ANALYSIS OF FOODS AND FEEDING STUFFS.*

Preparation of Sample.

The substance is to be ground and passed through a sieve with circular holes 1 m.m. in diameter.

Determination of Moisture.

Dry from 2 to 3 grms. of the substance for five hours, at the temperature of boiling water, by passing a current of dry hydrogen through the sample. If the substance be held in a glass vessel the latter should not be in contact with the boiling water.

Determination of Ash.

Char 2 to 3 grms. of the substance and burn to whiteness at the lowest possible red heat. If a white ash cannot be obtained in this manner, exhaust the charred mass with water; collect the insoluble residue on a filter, burn,

* Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (American) at its Meeting at Chicago, August, 1893.

add this ash to the residue from the evaporation of the above aqueous extract, and heat the whole to a low redness till the ash is white.

Determination of Ether Extract.

Extract 2 to 3 grms. of the substance dried as for the determination of the moisture, with anhydrous and alcohol-free ether, sixteen hours. Dry the extract, by exposure to the full heat of boiling water, to constant weight.

Alternate Method for Ether Extract.

In determining hygroscopic water, as above, continue the drying until the loss of weight in thirty minutes is reduced to 1 m.grm. or less; extract the dried substance for sixteen hours as directed, dry again, and give loss of weight as ether extract.

Anhydrous Ether.—To prepare the anhydrous alcohol-free ether required for estimation of fat, take any of the commercial brands of ether, wash with two or three successive portions of distilled water, add sticks of solid caustic soda or potash until most of the water has been abstracted from the ether. Carefully cleaned metallic sodium, cut into small pieces, is now added until there is no further evolution of hydrogen gas. The ether thus dehydrated must be kept over metallic sodium, and should be only lightly stoppered in order to allow any accumulating hydrogen gas to escape; and it may be drawn off with a pipette as required.

Crude Protein.

Determine nitrogen as directed for nitrogen in fertilisers and multiply the result by 6·25 for the crude protein.

Determination of Albumenoid Nitrogen (Stutzer's Method).

To 0·7 to 0·8 grm. of the substance add 100 c.c. of water in a beaker, heat to boiling, or in the case of substances rich in starch heat on the water-bath ten minutes, add a quantity of cupric hydrate mixture containing 0·5 to 0·6 grm. of the hydrate, stir thoroughly, filter when cold, wash with cold water, and put the filter and its contents into the concentrated sulphuric acid for the determination of nitrogen. The filter papers used must be practically free of nitrogen. Add sufficient potassium sulphide solution to completely precipitate all copper and mercury. If the substance examined consist of seed of any kind, or residues of seeds, such as oil-cake or anything else rich in alkaline phosphates, add a few c.c. of a concentrated solution of alum just before adding the cupric hydrate, and mix well by stirring. This serves to decompose the alkaline phosphates. If this is not done, cupric phosphate and free alkali may be formed, and the protein-copper may be partially dissolved in the alkaline liquid.

Cupric Hydrate.—Prepare cupric hydrate as follows:—Dissolve 100 grms. of pure cupric sulphate in 5 litres of water, and add 25 c.c. of glycerol; add dilute solution of sodium hydrate until the liquid is alkaline; filter; rub the precipitate up with water containing 5 c.c. of glycerol per litre, and then wash by decantation or filtration until the washings are no longer alkaline. Rub the precipitate up again in a mortar with water containing 10 per cent of glycerol, thus preparing a uniform gelatinous mass that can be measured out with a pipette. Determine the quantity of cupric hydrate per c.c. of this mixture.

Determination of Crude Fibre.

(1). *In Feeding-stuffs poor in Starch.*—Extract 2 grms. of the substance with ordinary ether, at least nearly completely, or take the residue from the determination of the ether extract. To this residue, in a 500 c.c. flask, add 200 c.c. of boiling 1·25 per cent sulphuric acid; connect the flask with a return-flow condenser, the tube of which passes only a short distance beyond the rubber stopper into the flask. Boil at once, and continue the boiling for thirty minutes. A blast of air conducted into the flask may serve to reduce the frothing of the liquid. Filter, wash thoroughly with boiling water until the washings are no longer acid; rinse the substance back into the same flask with 200 c.c. of a boiling 1·25 per cent solution of sodium hydrate at least almost free from sodium carbonate; boil at once, and continue the boiling for thirty minutes in the same manner as directed above for the treatment with acid. Filter in a Gooch crucible, and wash with boiling water till the washings are neutral; dry at 110°, weigh, incinerate completely, and give the loss of weight of crude fibre.

The filter used for the first filtration may be linen, one of the forms of glass-wool or asbestos filters recommended in the last report, or any other form that secures clear and reasonably rapid filtration. The solutions of sulphuric acid and sodium hydrate are to be made up of the specified strengths accurately by titration, and not merely from specific gravity.

(2). *In Feeding-stuffs rich in Starch.*—Proceed as under (1), using 2·5 per cent acid and alkali in place of the solution of 1·25 per cent strength.

THE CENTENARY COMMEMORATION OF LAVOISIER.

In his memorial lecture on Lavoisier, delivered at the Collège de France, May 7th, 1836, a hope was expressed by Dumas "that there may be erected to the memory of Lavoisier a monument which to posterity shall express our profound admiration for his genius and our lasting sorrow for his premature death."

Voices have been raised not only in France, but even in America, calling on the chemists of the world to unite in erecting such a memorial. This memorial must naturally be placed in Paris, the city which was irradiated by his genius and his discoveries and polluted by his *quasi*-judicial murder. By furnishing a site for such a monument she will in some measure atone for her error of the last century, just as Rome has done for the murder of Giordano Bruno. It is idle to contend that Lavoisier has no right to rank as a martyr of science, since he suffered not as a *savant* but as a *fermier général*. The suppression of the Academy and the exclamation that the Republic had no need of chemists show that the men who then dominated France were swayed by a diffused spirit of hatred to Science.

Nor should international jealousies interfere with the projected commemoration. The glory of Lavoisier and the importance of his life work are not dimmed by the fact that Priestley and Scheele were acquainted with oxygen prior to the great French genius. He saw the meaning of the facts which they failed to perceive. Hence he is called by Dr. Hinrichs the "Copernicus of chemistry."

As Berthelot most rightly says:—"That which we have a right to admire, that which the universal judgment of the civilised world with every day hallows more and more, is the positive work which he has accomplished; namely, the final erection, upon a permanent basis, of one of the fundamental sciences, Chemistry. No work in the history of civilisation is greater, and therefore the name of Lavoisier will live for ever in the memory of humanity."

May we not here express the earnest hope that British chemists will not fail to take a large and honourable share in so worthy a movement?

Eggertz Colour Test.—Mr. H. Joshua Phillips, F.I.C., finds that if translucent gelatin paper of a greenish yellow tint be used between the carbon tubes and an ordinary gas flame, the green colour often observed with mild steels is eliminated, and much smaller quantities of carbon can thus be determined.

ON THE ORIGIN OF GOLD NUGGETS.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

From time to time various theories have been put forth to account for the existence of alluvial gold and nuggets, *i.e.*, other than the old and generally accepted one, viz., that such gold has been derived or set free from mineral veins and rocks by the ordinary processes of disintegration and denudation.

The one first propounded by Mr. A. R. C. Selwyn, C.M.G., F.R.S., when Government Geologist to Victoria, has always interested me, and within the last two years I have been able to make some experiments bearing upon the matter, but before stating the results I will refer briefly to some of the theories above referred to.

Simpson Davison advanced a theory ("The Discovery and Geognosy of Gold Deposits in Australia," p. 132, London, 1860) "that alluvial or placer deposit gold has been distributed and deposited horizontally by means of an igneous liquid or perishable lava, and that quartz veins as well as some other dykes traversing constants had been the fissures of discharge,—the only unchanged existing solid remains of the ejected matter being gold, quartz, and some few other minerals besides clays and ferruginous earth." He advanced the theory because the alluvial or placer deposit gold has often a fused appearance, and the metallic grains frequently present ragged and irregular surfaces, such as must have been destroyed by abrasion. He also gives other reasons, but they are equally valueless and unimportant.

Mr. C. S. Wilkinson, F.G.S., formerly Government Geologist of New South Wales, refers in a paper read before the Royal Society of Victoria, September 11th, 1866, "On the Theory of the Formation of Gold Nuggets in the Drift," p. 11, to Selwyn's hypothesis, viz.:—"That nuggets may have been formed, and generally that particles of alluvial gold may gradually increase in size through the deposition of metallic gold (analogous to the electroplating process), from the meteoric waters which circulate through the drifts, and which must have been, during the time of our extensive basaltic eruptions, of a thermal and probably of a highly saline character, favourable to their carrying gold in solution," and states that "Daintree had on one occasion prepared for photographic use a solution of chloride of gold, leaving in it a small piece of metallic gold undissolved. Accidentally, some extraneous substance, supposed to be a piece of cork, had fallen into the solution, decomposing it, and causing the gold to precipitate, which deposited in the metallic state, as in the electroplating process, around the small piece of undissolved gold, increasing it in size to two or three times its original dimensions." Wilkinson then made certain experiments to test Daintree's theory. "Using the most convenient salt of gold, the terchloride, and employing wood as the decomposing agent, in order to imitate as closely as possible the organic matter supposed to decompose the solution circulating through the drift, I first immersed a piece of cubic iron pyrites taken from the coal formation of Cape Otway, and therefore less likely to contain gold than other pyrites. This specimen (No. 1) was kept in a dilute solution for about three weeks and is completely covered with a bright film of gold."

He also used galena, copper, and arsenical pyrites, antimony (*i.e.*, antimonite?), molybdenite, zinc blende, and wolfram, with similar results. Brown iron ore only gave a deposit of gold powder. He found that when iron pyrites was tried with metallic copper, zinc, and iron, the gold was only deposited as a fine powder at the bottom of the vessel, and came to the conclusion that organic matter was necessary to form a coherent coating of gold on the nucleus, for without the presence of wood, or similar organic matter, he found that the six sulphides were unaltered.

In his second experiment with iron pyrites, he found that the gold was deposited on it in a mammillary form, analogous to that presented by the surface of nuggets.

To sum up Wilkinson's paper, his points are—(1) that gold is deposited upon sulphides in the presence of organic matter; (2) that the organic matter is essential; (3) that the coating is mammillary in some cases; (4) that gold is probably present in solution in mineral waters; (5) that nuggets are purer than vein gold, and that this may be due to the nuggets having been deposited *in situ* from a solution of gold.

The next to take up the subject was Mr. J. Cosmo Newbery, in a paper "On the Introduction of Gold to, and the Formation of Nuggets in, the Auriferous Drifts" (*Trans. Roy. Soc. of Victoria*, 1868, p. 52). In this he admits that some nuggets and alluvial gold may be derived from the denudation of reefs, but points out that the largest masses are sometimes found at great distances from the reefs and in the sand overlying the gravel, both of which are inexplicable when the very great specific gravity of gold is taken into account. He also states that the presence of gold in pyrites which has replaced the roots, branches, and stems of recent trees, is a proof of the existence of gold in meteoric waters of the Tertiary Times.

He quotes Selwyn's hypothesis, and Selwyn and Ulrich ("Physical Geography, Geology, and Mineralogy of Victoria, 1866) to the effect that all the large nuggets have been found on the western gold fields where extensive basaltic eruptions have taken place, while on the eastern and northern fields, where basaltic rocks are wanting or only of limited extent, the gold is usually fine, and nuggets of more than one ounce are rare. He also states that Bischof has found gold sulphide to be soluble in pure water, and he has suggested that it may occur in that form in meteoric waters.

Newbery dissolved some gold sulphide in an alkaline bicarbonate, and found that when a cube of pyrites and a chip of wood were introduced that small irregular grains of gold were deposited, and states that the gold is not deposited without the organic matter (*i.e.*, the wood).

Newbery repeated and confirmed Wilkinson's experiments. Newbery points out that there is little proof in nature of pyrites having acted as a nucleus; it carries gold both internally and attached externally, but we do not meet with *gilded pyrites* such as are obtained in laboratory experiments, and that in nature the two appear to have been deposited together.

Newbery, out of one hundred samples of pyrites found none with any coating of gold, such as is obtained experimentally, but it was present in irregular grains and small octahedral crystals; in exceptional cases pieces of gold were found projecting, but all proved that the pyrites had not formed a nucleus for the gold, but the reverse has been the case in the mojority of instances, *i.e.*, the gold has been deposited first; and he suggests that the gold may have been deposited first in the drift wood; as seen when organic matter, flies, &c., fall into a gold solution, and the pyrites afterwards deposited around it.

He also refers ("Laboratory Report," Melbourne, 1876) to Daintree's discovery of an enlarged fragment of gold in a bottle containing chloride of gold, and states that "Ulrich, who was present when Daintree discovered the enlarged piece of gold, says that the original piece was a small fragment which remained undissolved after making some chloride and the bottle was closed with a cork; when again observed the solution was colourless and the fragment of gold of such a size that it could not be removed from the bottle through the narrow neck."

Newbery, like Skey, found that hammered pieces of gold did not increase in size, but he had little doubt of others with a rough or natural surface doing so.

Mr. Newbery was followed by W. Skey, F.C.S., Analyst

* A Paper read before the Royal Society of New South Wales, September 6, 1893.

to the Geological Survey of New Zealand, in a paper "On the Reduction of certain Metals from their Solutions by Metallic Sulphides, and the Relation of this to the Occurrence of such Metals in a Native State" (*Trans. N. Z. Inst.*, 1870, p. 226). Mr. Skey also repeated Wilkinson's experiments, and obtained the deposits of gold on various sulphides and arsenides, and further found that the presence of organic matter is quite unnecessary for bringing about the deposition of gold upon the above minerals. He also found that silver nitrate and acetate, and the salts of one or more of the platinum group of metals, are reduced by the metallic sulphides and arsenides. He points out that the metallic sulphides possess much greater reducing power than organic matter, and that a single grain of iron pyrites will reduce $8\frac{1}{8}$ grains of gold. And that although organic matter may have had a share in the reduction of gold, he is of opinion that the greater portion of the deposits—especially the deep-seated ones—have been due to the deoxidising effects of pyritous minerals.

In a succeeding paper, "On the Electromotive Power of Metallic Sulphides" (*Trans. N. Z. Inst.*, Nov. 12, 1870, p. 232), Mr. Skey describes experiments which he made to show that when such sulphides as pyrites and galena are placed in dilute acids or saline solutions and connected by a platinum wire, the current generated is sufficient to throw down gold in separate vessel from its chloride. He points out from these experiments and Mr. Fox's statements as to the existence of currents of electricity in the earth's crust, that each pyritous vein or mass with its surrounding walls and exciting solutions may constitute a true voltaic pair on a grand scale.

A third paper by Mr. Skey is entitled "On the Mode of Producing Auriferous Alloys by Wet Processes" (*Trans. N. Z. Inst.*, 1872, p. 370). He states, amongst other matters, "that when chloride of gold is added to an alkaline argentiferous solution of this nature (silver chloride in *alkaline* chlorides; silver chloride in either acid or neutral solutions is not reduced by iron pyrites), such mixed solution is capable of depositing the metals contained in it in the form of coherent alloys upon metallic sulphides;" also, that such alloys can be formed by voltaic action. Further, "that as the water permeating rocks is usually alkaline, it seems probable that native alloys of gold and silver have been deposited from alkaline solutions by the metallic sulphides."

He further remarks that many substances will reduce gold from solution, but the only common ones likely to occur in the interior of rocks are ferrous sulphate, organic matter, and the metallic sulphides; these also reduce metallic silver from certain of its solutions, but only the sulphides will reduce the two metals simultaneously and throw them down in coherent forms.

Mr. Skey continued his investigations, and published still further results in the following paper—"Critical Notes upon the Alleged Nuclear Action of Gold upon Gold Reduced from Solutions by Organic Matter" (*Trans. N. Z. Inst.*, 1872, p. 372). In this paper Mr. Skey gives the results of his attempts to confirm Daintree's and Wilkinson's experiment, but, as he says, unsuccessfully; he accordingly describes minutely the methods which he adopted, and found that when a weighed piece of sheet gold was placed in a dilute solution of sodium chloraurate with organic matter until all the gold was precipitated, that the piece of gold only increased in weight 0·0005 grm. and by calculation he found that no more gold in proportion was deposited upon the gold plate than upon the sides and bottom of the glass vessel, and even the surface of the liquid itself—the experiment was repeated four times. He points out that the conditions in Daintree's accidental result are so vague and uncertain that it is impossible to credit the organic matter with producing the phenomena described. Neither the volume nor the weight of the undissolved gold was taken, hence he considers that the statement that after some time the fragment of gold had increased in size is of but little value, as it depended entirely upon the eye memory of the original size of the gold particle, and an ocular estimate of its increased dimensions.

In his next communication, "On the Formation of Gold Nuggets in Drift" (read before the Wellington Philosophical Society, October 23, 1872, *Trans. N. Z. Inst.*, vol. v., pp. 377—383), Mr. Skey says:—"We cannot avoid the conclusion that gold is now being deposited and aggregated in many of our drifts, and that such depositions have been going on from remotest times." He thinks that this gold is derived from the metal disseminated through slate, sandstone, or schist rocks rather than from that of our reefs, and that we may reasonably suppose it is present as sulphide and is brought into solution by alkaline sulphides, from which it is again eventually re-deposited as nuggets, &c., by the reducing effects of metallic sulphides—a mass of iron pyrites only two pounds in weight being sufficient to cause the deposition of a nugget such as the "Welcome," weighing 184 pounds troy.

Sir Rod. J. Murchison ("Siluria," 5th Edition, 1872, p. 465), after referring to Mr. A. C. Selwyn's suggested explanation as to the formation of nuggets, and to Mr. Wilkinson's experiments, says that he "prefers to remain in his old belief, that the large nuggets found in the drift are simply the reliquiæ of the chief masses of gold which once occupied the uppermost parts of the reefs, and that like the blocks of many an ancient conglomerate, they have been swept from the hilltops into adjacent valleys by former great rushes of water."

Mr. Brough Smyth, F.G.S., in his work on "The Gold Fields and Mineral Statistics of Victoria," 1869, p. 361, discusses the origin of nuggets, and points out that most of the large nuggets have had a great quantity of quartz adhering to them or intermixed with them, clearly indicating that the nuggets must have come from a quartz reef, or else the gold and quartz must both have been deposited together from meteoric water in the drift.

In Mr. W. Birkmyre's list of nuggets quoted by Mr. Brough Smyth, he says of the Welcome nugget, weight 184 pounds 9 ozs. (troy), that it was apparently water-worn, and contained about 10 pounds of *quartz*, clay, and oxide of iron.

The Blanche Barkley, which weighed 145 pounds 3 ounces, apparently contained 2 pounds of *quartz*, clay, and oxide of iron.

The next in his list weighed 134 pounds 11 ounces, contained dark coloured quartz.

In fact, he mentions the association of quartz with nearly all the very large nuggets, and expressly states that many of the smaller ones were free from quartz; as we might naturally expect.

Brough Smyth remarks that "much stress is laid on the fact that nuggets are sometimes found at a considerable distance from a quartz reef;" but it may be that the reef from which the nugget has been set free may have been completely denuded away; its matrix need not necessarily have been the nearest now existing reef. He quotes Ulrich's remarks in support of Selwyn's hypothesis of the formation of gold nuggets *in situ* in alluvial deposits ("Notes on the Physical Geography, Geology, and Mineralogy of Victoria," by Alfred R. C. Selwyn and George Ulrich, Melbourne, 1866, p. 43), but points out that if such is the case in the present day, then the older sedimentary rocks ought, from the greater lapse of time, to contain large masses of gold. Moreover, large nuggets are not confined to deep leads, but many have been found only a few inches below the surface. He also says that the statement that all the large nuggets have been found on the western gold fields, where basaltic eruptions have been prevalent, is erroneous; many large nuggets have been found remote from basaltic areas, and Mr. Birkmyre's list shows that the fields most remote from basaltic areas have produced the most large nuggets; in Gippsland, if not large, they are numerous.

Mr. G. Attwood, in a paper on "Gold from Guayra,

Venezuela, South America" (*Journ. Chem. Soc.*, London, 1879, p. 427), concludes, from an examination of one particular specimen, that gold nuggets do gradually increase in size owing to the accumulation of fresh particles of finely precipitated gold.

Prof. Whitney, in a paper—"The Auriferous Gravels of the Sierra Nevada of California," Cambridge, U.S.A., 1880—says that "it does appear as if there was some truth in the idea that the finding of large pieces of gold in the gravel is not justified by what we see of the occurrence of the metal in the quartz. It is certain, at all events, that the form of the ordinary nugget is something different from that which is offered by the gold as originally deposited. In quartz it is either quite invisible or else it is scaly, foliated, filamentous, arborescent, or crystalline, quite unlike the rounded and smooth or flattened pieces met with in alluvial deposits." He, however, points out that this difference could be produced by attrition, and he thinks it highly improbable that the masses of gold in gravel could be enlarged by any chemical influence.

The bark of some of the tree trunks found buried in the blue gravel (Cal.) is largely replaced by iron pyrites, and this is rich in gold; "hence we cannot deny that some gold has been deposited in the placers from solution, but this certainly does not include the nuggets and gold dust." He also says: "If the gold of placers were deposited from solution, we should necessarily find much of it crystallised and forming strings and sheets running through the porous material; whereas, as a matter of fact, crystals are never found in placer gold, nor are sheets or threads. Scales, grains, pebble-like nodules, round battered masses, these are what we find."

(To be continued).

THE ACTION OF CYANIDE OF POTASSIUM ON GOLD AND SOME OTHER METALS AND MINERALS.*

By G. A. GOYDER, Adelaide, S.A.

Sometime since Mr. J. V. Parkes, the Inspector of Mines, asked me for some information as to the interference caused by copper ores in the MacArthur-Forrest process of extracting gold. On consulting the text-books but little could be found bearing on this subject, and this having been cited in some recent articles by Messrs. Butters and J. E. Clennell on "The Chemistry of the Cyanide Process" in the *Engineering and Mining Journal*, liv., 1892, 391—417, it is not necessary for me to recapitulate it here.

In the absence of a full library of chemical literature, it was impossible to make such a complete search as was desirable before starting work, and this must be my excuse for bringing forward some matter which may not be entirely new.

Messrs. Butters and Clennell, in the articles above quoted, have gone very thoroughly into the losses involved in the cyanide process for extracting gold, and indicated with what classes of ore it may be profitably used; but they have left untouched some points on which I had been experimenting some time before their papers were seen here, and which also bear more or less on this process.

It has not been possible with the limited time and material at my disposal to make anything like an exhaustive analysis of the many complicated reactions which presented themselves during the research, and I feel that it is only the general interest which is now being taken in the cyanide process that justifies me in bringing forward such a fragmentary contribution.

* From the *Transactions of the Australasian Institute of Mining Engineers*, vol. i. Meeting held in April, 1893.

The first experiments undertaken were to test the solvent action of cyanide of potassium on some of the more common minerals of copper. A report of the results of these experiments was forwarded to Mr. Parkes last year, and is reproduced here.

The Action of some Copper Minerals with One Per Cent Cyanide of Potassium Solution.

In carrying out these experiments the minerals used were not perfectly pure, but at the same time were sufficiently free from associated minerals to remove any doubt as to the action. They were crushed and passed through a sieve containing 30 holes to the linear inch. The cyanide of potassium used contained 91·5 per cent of pure KCN, and a solution of this was made by dissolving one part in 100 parts of water; 10 parts of the mineral were placed in a stoppered bottle, and 100 parts of the cyanide solution added. The bottles were kept screened from the light and shaken vigorously six times at intervals of an hour, then allowed to stand all night, the clear liquid decanted and passed through a filter and tested for copper and for free potassium cyanide, with the following results:—

Mineral.	KCy used in grains per gallon.	KCy saturated by mineral in grains per gallon.	Cu dissolved by KCy in grains per gallon.	KCy left free in grains per gallon.
Azurite	700	600	142·7	100·0
Malachite . ..	700	693·5	148·4	6·5
Native copper..	700	577·4	159·6	122·6
Copper glance .	700	700·0	43·6	nil
Copper pyrites .	700	335·1	33·6	364·9
Iron pyrites ..	700	71·5	4·5	628·5
Quartz	700	43·8	—	656·2

The quartz used was an ordinary sample of free milling quartz, and was included to test the action on a sample not containing copper or other disturbing mineral.

The azurite and malachite were freely dissolved by the cyanide, the action being approximately normal, as expressed by the formula of the double cyanide,—

$$CuCy_2 + 2KCy,$$

one atom of copper saturating four of KCy. The whole of the cyanide would doubtless have been thus acted on if the action had been prolonged.

The action of the native copper is given further on. The copper glance had the most energetic action of all on the cyanide, which it quite neutralised; at the same time very much less copper went into solution than with the carbonates, and this reaction will be further studied.

MacArthur-Forrest, in "The MacArthur-Forrest Process of Gold Extraction," *Journ. Chem. Trade*, 1890, 269, state that "sulphides of copper, zinc, and iron artificially prepared are readily acted on by cyanide of potassium, but not the mineral." The mineral sulphides of copper with which I have experimented are certainly very readily acted on. The sulphides of zinc and iron are not acted on, whether mineral or artificial,* as Mr. MacArthur appeared to know, as regards zinc at least, where he states that "if zinc be present (in a cyanide solution), this should be removed by the addition of ammonium sulphide" (*Journ. Chem. Trade*, 1890, 190).

The copper pyrites acted in a similar manner to the copper glance, but much less energetically.

The iron pyrites, a sample from the Alma and Victoria gold mine, acted also in the same manner as the copper glance, the action being apparently proportional to the small quantity of copper present, and with pure iron pyrites the action would doubtlessly be nil.

In order to test the cyanide which had been saturated by a cupreous mineral against the simple cyanide of potassium, the following experiment was made:—

* This statement requires further experimental proof. The solution of sulphides by, and their precipitation from, cyanide solution require thorough investigation.

Gold taken.	Gold dissolved by 1 per cent KCy.	Gold taken.	Gold dissolved by 1 per cent KCy shaken with malachite.
2412	130	2845	11
2724	110	2282	4

Showing that the cyanide of potassium loses its power of dissolving gold when it has been saturated by a cupreous mineral.

There are doubtless other minerals which would act in the same manner as those of copper mentioned above, among which would probably be some compounds of nickel, cobalt, and cadmium, but as these are not of frequent occurrence with gold no experiments have yet been made with them.

In the above experiment the gold used was in the form of wire about 1-70th of an inch thick, and the cyanide was allowed to act on it for twenty-four hours; during this time about 1-20 of the gold was dissolved; so that it it is evident, as there was a large excess of cyanide present, that the cyanide process, like the chlorine processes, is not suitable for the treatment of coarse gold.

Gold.

Mr. MacArthur states (*loc. cit.*) that he "never could find that the presence of oxygen was necessary either to dissolve gold by itself or from ores by cyanide. . . . The equation shows that either oxygen must be absorbed or hydrogen evolved . . . but I think the latter the more probable.

The above quotation induced me to detail the following experiments, although Elsner long since showed the necessity of the presence of oxygen, but his paper on the subject is not accessible here.

Three gold leaves were placed with an aqueous solution of 6 per cent of cyanide of potassium (6 per cent KCyAq) in a test-tube, and inverted over a basin containing the same solution on July 25, 1892, as in Fig. 2.

On July 26, 1892, the leaf at the bottom, *i.e.*, nearest the outer air, was dissolved, while that at the top was not sensibly affected. More gold was shaken to the bottom by gently rotating the tube.

July 30, 1892—Gold near bottom dissolved, near top not dissolved; more shaken down.

August 1, 1892—A similar result.

August 3, 1892—A similar result, but no more gold was shaken down. The tube was examined from time to time till October 14, 1892, when the gold at the top still appeared of the same bulk and substance as on August 3. A little oxygen was then introduced into the tube; the disturbance caused most of the gold leaf to fall to the bottom at once, that which remained near the top slowly but continually dissolved and broke away, until in a short time, less than an hour, only a little was left above the surface of the solution. By means of a bristle a small piece was replaced near the top of the solution at 3.15 p.m.; by 5 p.m. this piece had all dissolved.

October 15, 1892—Another gold leaf added to the same solution, and nearly all of it held by means of a bristle at the top of the solution near the oxygen.

October 17, 1892—Most of the gold dissolved.

October 17, 1892—Two leaves of gold placed in a test-tube and held in position by means of bristles, 6 per cent KCyAq poured in and the tube inverted, and 2 to 3 c.c. of CO_2 introduced.

November 7, 1892—Gold still at top near CO_2 and apparently intact, 2 to 3 c.c. of oxygen introduced, when the gold all dissolved in half an hour.

Numerous other experiments were made, both with gold and silver, but all with the same result, and all tending to prove that these two metals only dissolve in KCyAq in the presence of oxygen, and that hydrogen is never evolved. One case may be mentioned in which a coil of silver wire was placed in an unstoppered bottle of 6 per cent KCyAq: near the bottom of the bottle the wire appeared unchanged, but near the surface where the oxygen from the air could be absorbed, the wire was deeply pitted, and in one place eaten right through and broken away.

With a weaker, 1 per cent, solution the action was the same.

(To be continued).

PROCEEDINGS OF SOCIETIES.

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

The Anniversary Dinner of this Institute took place on Friday, May 25th, at St. James's Hall, under the chairmanship of Dr. W. J. Russell, F.R.S, the President of the Institute.

The guests included most of the leading chemists, physicists, and technologists of the country. We may mention in particular Lord Kelvin, P.R.S.; Sir F. A. Abel, Bart., F.R.S.; Professor A. Dupré, F.R.S.; Dr. E. Frankland, F.R.S.; Professor James Dewar, F.R.S.; Dr. Odling, F.R.S.; Prof. W. A. Tilden, F.R.S.; Prof. H. E. Armstrong, F.R.S. (President of the Chemical Society); Prof. J. Norman Lockyer. C.B., F.R.S.; Prof. Carrington Bolton; W. Crookes, F.R.S.; A. Giles (President of the Institute of Civil Engineers); Maj.-Gen. A. de Courcy Scott, R.E.; Sir J. Evans, F.R.S. (Treasurer of the Royal Society); E. C. C. Stanford (President of the Society of Chemical Industry); Dr. C. O'Sullivan, F.R.S.; Drs. Voelcker, Clowes, Ramsay, Thorpe, Thorne, Muter, Kellner, Luff, Spiller, &c.

After the usual loyal toasts had been duly honoured, Dr. Tilden proposed the Learned Societies. He gave a somewhat humorous sketch of the earlier days of the Royal Society, founded by Charles the Second for the promotion of natural knowledge. He referred to the apologetic tone of its history compiled by the Bishop of Rochester, when it was scorned by the "wits," denounced by the classicalists, and bemoaned by a section of the religious world as hostile to Christianity. After showing how the increase of intellectual activity had led to the formation of a number of other learned societies, who might be considered as subsidiary to, and co-operative with, the Royal, he combatted a popular error concerning the Institute of Chemistry. Though composed of learned men, it is not a learned society; it is a professional organisation not seeking to extend the limits of natural knowledge, but to ensure higher qualifications among chemists.

Lord Kelvin, President of the Royal Society, in acknowledging the toast, showed the error of supposing that the subsidiary learned societies would leave nothing for the Royal Society to do. So far is this from being the case, that the Council, President, and Secretaries, and, above all, the Treasurer, are becoming more and more perplexed how to deal with the growing mass of papers poured in upon them, all containing matter worth insertion in the *Proceedings* or in the *Philosophical Transactions*, but which the lack of funds excluded! For this state of things Lord Kelvin declared himself unable to propose any adequate remedy. It seems desirable that, whilst experimental details are best left to the special societies, all grand generalisations, and all researches which overstep the limits of any one science, should be recorded in the *Philosophical Transactions*.

In succession followed toasts to the "President and Institute of Chemistry," proposed by Sir J. Evans, K.C.B., F.R.S., and replied to by the President, Dr. W. J. Russell, F.R.S.; the "Past Presidents," proposed by E. C. C. Stanford, and replied to by Dr. E. Frankland, F.R.S.; and, lastly, "The Guests," proposed by the

Treasurer, and replied to by Prof. J. Norman Lockyer, C.B., F.R.S.

The large and influential gathering then dispersed, fully sympathising with the objects and prospects of the Institute of Chemistry.

SOCIETY OF CHEMICAL INDUSTRY.

A MEETING of the Nottingham Section of the Society of Chemical Industry was held at University College, Nottingham, on Wednesday, May 23rd. The Chairman, Mr. J. M. C. Paton, presided, and

A paper by Messrs. SCHWEITZER and LUNGWITZ, of New York, "*On Commercial Analysis of Lard*," was read by the Hon. Secretary, Mr. LLOYD WHITELEY.

The authors speak of the great progress made of late in compounding lards, and state that the principal adulterants are cotton-seed oil, cotton oil stearine, lard stearine, and oleostearine. They consider that the following six tests, taken together, and in order, are the most valuable:—

1. The test with phosphomolybdic acid (Sonnenschein's reagent).
2. Milliau's nitrate of silver test.
3. Hübl's iodine absorption.
4. Maumené's sulphuric acid test.
5. The crystallisation point.
6. The microscopical appearance.

Details are given for carrying out the phosphomolybdic test; stress is laid on the necessity of acid of constant strength in Maumené's reaction, and it is proposed to shorten the time required for the iodine absorption by means of heating.

The paper was criticised by Mr. RIMMINGTON, who showed that little reliance could be placed upon the different crystalline appearances.

Mr. ALLEN objected on principle to any colour reaction, such as those with phosphomolybdic acid and nitrate of silver, because they depend upon unknown factors; and he also thought the proposed change in Hübl's method too arbitrary.

Prof. CLOWES also gave an instance to show how utterly unsatisfactory Maumené's test might be.

NOTICES OF BOOKS.

The Tannins: a Monograph of the History, Preparation, Properties, Methods of Estimation, and Uses of the Vegetable Astringents. With an Index to the Literature of the Subject. By HENRY TRIMBLE, Ph.M., Professor of Analytical Chemistry in the Philadelphia College of Pharmacy. Volume II. The Tannins of Oak-bark, Mangrove, Canaigre, Chestnut. London and Philadelphia: Lippincott Co. 1894.

THE author tells us in his preface that he has examined the astringent principles of nine species of oaks, and one species each of mangrove, canaigre, and chestnut. In the former volume he discussed the tannins as a class, and the pathological tannins of gall-nuts.

The tannins of catechu, myrobalans, sumac, the wattle-barks, &c., do not receive an extended notice. This is the more to be regretted since these substances, if less interesting to the tanner, are more important to the dyer. Oak-barks, mangrove, and canaigre concern the colour chemist but little. The same may be said of the chestnuts, which furnish a tannin sometimes encountered where it is unwelcome, *i.e.*, in the sophistication of extracts of logwood.

The oak-barks are certainly here dealt with in a very thorough manner. Their reactions, their localities, their botanical identification are all carefully and elaborately expounded.

For the analysis of the oak-barks the author gives the preference to "the practical, but rather unscientific hide-powder method."

Chestnut-wood is admittedly poor in tannin, Mr. Trimble finds in the air-dried chips 7·85 per cent. and in the bark only 7·31.

The ultimate composition of the tannins is far from identical in the gallotannic acid and in the tannins of chestnut-wood and bark, and in that of sumac the carbon is 52 per cent. In pomegranate-bark it is 50. In the tannins of oak-bark, mangrove, canaigre, rhatany, kino, catechu, and tormentil it ranges, according to various chemists, from 58·10 to 59·79.

As far as it extends, this work is valuable. But we should like to see all the tanniferous products of commerce, wherever growing, examined in an equally careful manner.

Systematic Survey of the Organic Colouring Matters. By Drs. C. SCHULTZ and J. JULIUS. Translated and Edited with Extensive Additions by ARTHUR G. GREEN, F.I.C., F.C.S. London and New York: Macmillan and Co. 1894. 205 pp.

THIS work must be welcomed by all persons connected with our tinctorial industries. The tables give in eight parallel columns the commercial names of the dye-wares, their scientific names, their empirical formulæ, methods of preparation, date of discovery, name of discoverer, with the patents for their manufacture, and the literature in which they are more fully described. Lastly, we find their appearance, their behaviour with reagents, their shades and dyeing properties, and the method of their employment. The amount of useful information thus tabulated is truly wonderful. We must, however, ask whether "invention" and "inventor" would not have been terms preferable to "discovery" and "discoverer." We "discover" what has always existed in nature, but has been previously unknown to man. We "invent" what has had no previous existence as such, though its materials have existed from time incalculable.

On examining the table we are further struck with the unpleasant fact that only a very small proportion of the dye-wares here mentioned are of British origin. Another noteworthy fact is the extreme rarity of tinctorial compounds invented abroad, but patented in Britain. A still greater rarity, if possible, is to find any such patent being worked on British soil or being allowed to lapse. Thus our patent laws, as now carried out, exist not to facilitate the introduction of new arts into these realms, but to prevent such introduction. This question, however, cannot be here discussed. The editors have added some very important matter, that is, an account of the raw products, such as coal-tar and its leading constituents, benzene, toluene, xylene, naphthalene, anthracene, phenol, and cresol. Next follows a very valuable section on the intermediate products used in the manufacture of the ultimate tinctorial products.

Upon the whole the editors and the publishers may be most warmly congratulated on the important addition they have made to English technical literature.

Lectures on the Sanitation of Industries and Occupations. Published by the Sanitary Institute. London. 1893.

THE six Lectures reproduced in this volume were delivered under the auspices of the Sanitary Institute, with the view of enabling both masters and men to learn the practical application of sanitary principles to particular industries. They deal with (1) occupation and mortality; (2) mineral (non-metallic) dusts, the manufacture of pottery, &c.; (3) metallic dusts, cutlery, tool-making, and other metal trades; (4) textile manufactures, silk, cotton, woollen, and linen industries; (5) metallic poisons, lead, and arsenic; (6) the manufacture of alkalis and acids.

These do not, of course, cover the whole range of the subject, but it is intended to have a longer series this year.

Owing to the increased activity of factory inspectors, unhealthy trades, which for generations have been left alone, are attracting the attention of the authorities, and enquiries are being made with the object of ascertaining whether the enormous death rate in some of them cannot be prevented or reduced. The general consensus of opinion seems to be that, to a considerable extent, the remedies lie in the hands of the persons affected.

Dust is one of the chief causes of early death in many industries, and though its baneful effects could be obviated by the use of respirators, employers have found it almost a hopeless task to get their workpeople to wear them.

In other trades, such as wet-grinding, the difficulties to be overcome to improve the sanitary conditions of the workshops are much greater, the whole floor and atmosphere is saturated with moisture, and consequently the mortality from phthisis is extremely high. Employers are, however, becoming more alive to the necessity of improving the conditions of labour, and if the employés will only contribute to their own safety by exercising more care, the result cannot fail to be satisfactory to all concerned.

The Comprehensive Cash Book; and, the Income Tax made Easy. By W. CASTLEDINE. London: C. W. Page and Sons.

To record the fact that this is the eleventh year of publication of this Cash Book is a sufficient proof that it is largely used and appreciated. Besides being a "Cash Book," it teaches a very simple and useful system of book keeping, and gives very valuable information respecting the *legal* manner in which the income tax should be levied, and how to recover any excess that may have been paid.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 20, May 15, 1894.

M. Blondlot was elected correspondant for the Section of Physics *vice* Prof. von Helmholtz, who has been promoted to the rank of Foreign Associate.

Researches on the Increase of Crops by the Injection of Large Doses of Carbon Disulphide into the Soil.—Aimé Girard.—The author, in combatting the inroads of *Heterodera Schachtii* in a field of sugar beets in 1887, succeeded in destroying both the parasites and the beets. In 1888 wheat planted in the same fields flourished much better where the insecticide had been applied than elsewhere. A similar benefit was observed with other crops, especially potatoes and clover. All insects present in the soil were banished or killed, as also the earth-worms (a very doubtful benefit). The author admits that the quantities of carbon disulphide employed were beyond the limits of practical agriculture.

Physical Properties of Pure Nitrous Oxide.—P. Villard.—The vapour density was obtained by means of a Natterer's tube. The results at the temperatures from 0° to 36·3° ranged from 0·0870 to 0·338. The critical temperature of pure nitrous oxide is 38·8°, the critical pressure being 77·5 atm.

Stability of Dilute Solutions of Mercuric Chloride. Léo Vignon.—The changes produced with time in dilute solutions of mercuric chloride are chiefly due to the introduction of alkaline matter, whether by the water used in preparing the solution, or by the air, or by glass vessels containing the solutions. To these agencies must be added the influence of dust or of organic bodies, the contact of which reduce mercuric oxide and facilitates the precipitation of the mercury.

Chemical Function and the Constitution of Ethylacetylacetic Acid.—M. de Forcrand.—It appears certain that this acid has not a ketonic function. It must be a phenol with an open chain having the fundamental character of the phenols and presenting like all these compounds that acidity intermediate between the true acids and the alcohols which leads us to assimilate these substances to acids and their metallic derivatives to salts. The phenolic value is +39 cal., intermediate between that of the alcohols (+28 to +32) and that of the acids (acetic acid = +50·17).

A Comparative Study of the Isomeric Nitrobenzoic Acids.—Oechsner de Koninck.—The author has determined the coefficients of solubility for these three acids at temperatures equal to or below the ordinary temperature. He has also studied methodically the action of sulphuric and common nitric acid, in which they dissolve with a faint yellow colour, whilst the amido benzoic acids all three dissolve with a garnet-red colour in the monohydrated nitric acid. The action of fuming nitric acid differs little from that of ordinary nitric acid.

MISCELLANEOUS.

Mica.—We understand that Messrs. Wiggins and Sons, of 102, Minories, E.C., have again obtained the Admiralty contract for the supply of mica. This is the largest order that has ever been placed by this Department.

Appointment.—Dr. A. B. Griffiths has been appointed District Agricultural Analyst by the Peterborough County Council, and the appointment has had the approval of the Board of Agriculture.

Special Manures.—Messrs. W. H. and L. Collingridge will shortly publish a work entitled "Special Manures for Garden Crops," by Dr. A. B. Griffiths. The work contains an elaborate series of analyses of the ashes of plants.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Society of Chemical Industry, 8. "Experiments on the Strength of Leather" and "Note on the Colour of Brass," by W. G. Macmillan, F.I.C., F.C.S. "Distillation of Peat," by Dr. P. Dvorkovitch.
—— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 5th.—Royal Institution, 3. "The Modern Microscope: an Instrument for Recreation and Research," by the Rev. W. H. Dallinger, F.R.S.
WEDNESDAY, 6th.—Geological, 8.
THURSDAY, 7th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "Egyptian Decorative Art," by Prof. W. M. Flinders Petrie, D.C.L.
—— Chemical, 8. Ballot for the Election of Fellows. "The Nature of Phosphorescence," by Herbert Jackson, B.Sc. "The Crystallography of the Normal Sulphates of Potassium, Rubidium, and Cæsium," by A. E. Tutton. "The Boiling-points of Homologous Compounds, Part II.," by Dr. James Walker.
FRIDAY, 8th.—Royal Institution, 9. "The Newtonian Constant of Gravitation," by C. Vernon Boys, F.R.S.
—— Astronomical, 8.
—— Physical, 5. Discussion of the Paper by Mr. Baly and Prof. Ramsay, F.R.S., on the "Relations of Pressure, Volume, and Temperature of Rarefied Gases." An Exhibition of Photographs of Flames, by Capt. Abney, F.R.S.
SATURDAY, 9th.—Royal Institution, 3. "The Stage and Society," by Robert W. Lowe.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Separation of Iron and Tin.—As a chemist in an iron works I have had considerable difficulty with the following problem, and should be glad if you would kindly give me a little advice respecting it. The case is shortly as follows:—I have a hydrochloric acid solution containing much tin and little iron. The object is to separate the tin and obtain it as SnO_2 and throw the iron away. We do not wish to obtain the tin in the metallic state or to recover the hydrochloric acid.—H. W. B.

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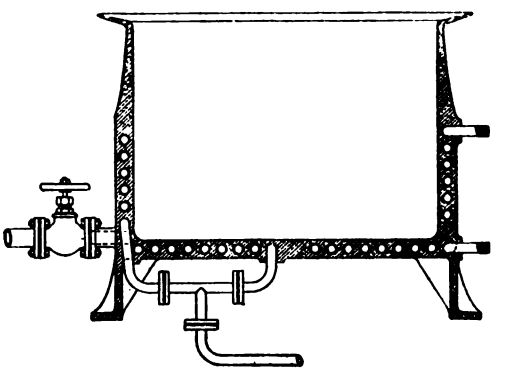

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says:—

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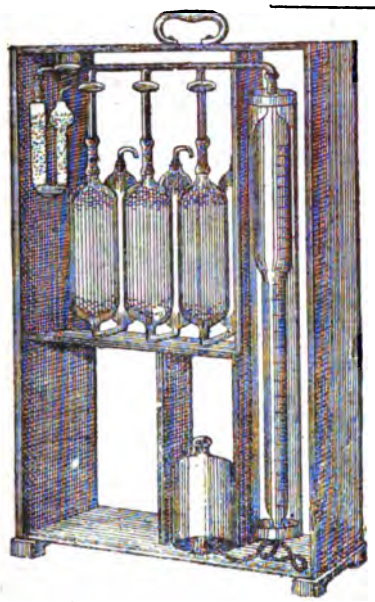

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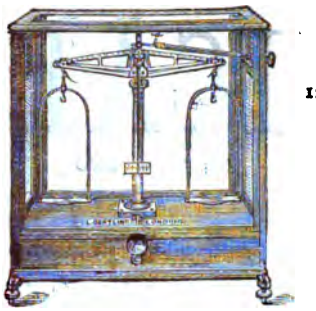

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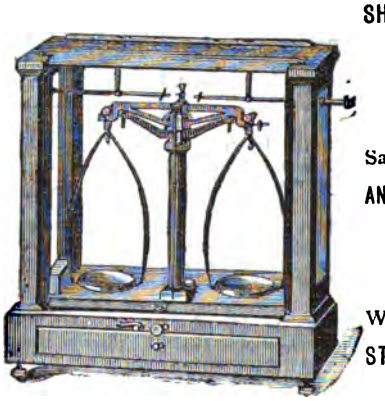

FIG. 3*a*.

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THE CHEMICAL NEWS.

Vol. LXIX., No. 1802.

ON THE ORIGIN OF GOLD NUGGETS.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

(Continued from p. 262).

Prof. J. S. Newbery, in a paper "On the Genesis and Distribution of Gold" (*School of Mines Quarterly*, iii., New York, 1881), does not support Selwyn's hypothesis. He points out that a mass of vein gold was obtained weighing 95½ pounds, and originally 140 pounds, from the Monumental Mine, Sierra Buttes, Cal., which proves that large masses do occur in veins as well as in the form of nuggets.

He thinks that the proportion of large masses from veins is quite equal to that from placers or alluvial deposits. The smaller proportion of silver in alluvial gold, he thinks, is accounted for by the greater solubility of silver in various solutions, and its consequent removal just as in the process of "pickling" by jewellers.

Other "nuggets" from veins might be cited, *e.g.*, a mass of gold and quartz celebrated as Dr. Kerr's "hundredweight of gold" was found in 1851 in the Meroo or Louisa Creek, River Turon, N.S.W., at a place now known as Hargraves. Although in three pieces when discovered, it apparently had formed one mass; the three pieces weighed 1¾ cwts. and yielded 106 pounds troy of gold. Another mass of gold and quartz which yielded 120 pounds of gold on being pounded with a hammer was found at Burrandong, near Orange, N.S.W., in 1858. Some very large masses of gold were found in Beyers and Holtermann's quartz reef at Hill End, N.S.W. From 10 tons of quartz 102 cwts. of gold were said to have been obtained. (A. Liversidge, "Minerals of N. S. Wales," p. 21, London, 1888).

Walter B. Devereux, E.M., in a paper "On the Occurrence of Gold in Potsdam Formation, Black Hills, Dakota (*Trans. Am. Inst. Mining Engineers*, 1881, p. 465), states that careful observation in the field and consideration of the facts have led him to reject the theory that the gold has been deposited in the conglomerates from solution, and he regards it as a purely mechanical constituent; but states, p. 471, that "the larger the grain of the alluvial gold the greater the amount of silver it contains."

Prof. Egleston, in his work upon "Metallurgy of Silver, Gold, and Mercury in the United States" (New York, 1887, vol. ii., p. 57) takes up the question of the origin of nuggets, and quotes a letter from Mr. Selwyn, 28th March, 1882, in which Mr. Selwyn stands by his original hypothesis as follows:—"The cause (*i.e.* of nuggets) was the percolation through the gold bearing strata of very large quantities of saline and acid thermal waters, during the period of great volcanic activity, which produced the basalts. This action accompanied, but to a great extent succeeded, the phenomena which produced the present placer deposits. This gold from meteoric waters deposited on that already in the sands produced the nuggets. He further states that his opinion is confirmed by the fact that large nuggets only are found in the western gold-fields, as at Ballaarat, Daisy Hill, &c., where immense basaltic eruptions had taken place all over the district. In the eastern and northern districts, as Gippsland, Ovens, &c., where streams of basalt occur only to a very limited extent, or are altogether absent, the gold is generally very fine, and nuggets over one ounce in weight are of the greatest rarity." Brough Smyth, however, states otherwise (see *ante*, p. 261).

Prof. Egleston urges that in cases where the "gold does come from the destruction of veins, the surfaces are rounded and worn smooth." . . . "This is in entire contradiction to the mammillary structure of the nuggets." . . . They would have been water worn on the outside, and the cavities "would have been in the condition in which they left the vein, and the edges of any crystals found there would have been sharp; while in the nuggets the mammillary form exists even where crystals or the commencement of crystallisation is observed, the edges of the crystals are very often blunted or rounded, showing both deposition and solution on these edges."

Egleston also urges, as others have done, that if the gold had come from the eroded rocks it should have the same composition as that of the veins of the district in which it is found; whereas, he says, it is well known that vein gold is usually poorer than the alluvial gold of the same district, *e.g.*—

	California.	Australia.	Transylvania.	Nevada.
Nuggets	800—980	992·5—966	—	—
Veins ..	730—860	—	600	333—554

Egleston states, "that the violence of the old placer currents was very much greater than that of the ordinary streams of these days," and that "if this were the whole process and no further action had taken place, the gold would have been found in the comminuted condition exclusively." Further, "that gold is, however, also found as nuggets, and in small particles in rocks which have never been disturbed from their original positions, but which have been decomposed to a considerable depth, and it then has the same mammillary form, occupying positions which make it evident that it must have been formed *in situ*, and never have undergone any abrasive action. The nugget found in 1828 in Cabarrus Co., N.C., which weighed 37 pounds, and also the one found in the valley of Taschku Targanka, near Miask, in Siberia, which weighed 96 pounds, were both found under such circumstances in a decomposed dioritic rock. In some few cases it has been definitely ascertained that the gold has been dissolved and precipitated in the decomposed rocks, for it has penetrated only just so far as the decomposition has allowed it, the yield in gold ceasing entirely at the point where the rock allowed no further filtration; while in other rocks of a more porous nature in the same district the gold has penetrated to a depth not yet ascertained."

"There is a tradition prevalent in all the shallow placer gold mines of the south, and in those of some other districts, to the effect that gold *grows* from the *seed* gold which is not extracted, so that every few years the tails of the old mines are re-worked, generally with a profit; the quantity separated each time, according to the local tradition, being in proportion to the length of time the material has remained undisturbed." This admits of an easy explanation, although Prof. Egleston does not offer one, viz., that the gold is, of course, not wholly removed by the ordinary processes of extraction, and some, although a smaller amount, is almost certain to be obtained by such successive treatment; moreover the material becomes more broken up by the further handling and weathering, and more gold is thus set free both mechanically and probably by chemical changes also.

He then cites, page 64, experiments of his own similar to Wilkinson's, Newbery's, and many others, to show that gold is precipitated from its solution as chloride by petroleum, cork, peat, leather, leaves, &c. The petroleum threw down long crystals of gold resembling Chester's hexagonal crystals, and the peat a mammillary mass resembling the form of nuggets.

He then tried, p. 65, the solubility of gold in solutions of salts; ammonium sulphate and chloride, potassium chloride and bromide, placed in sealed tubes with spongy

* A Paper read before the Royal Society of New South Wales, September 6, 1893.

gold for eight months gave no reaction; on heating them for five hours at 150° to 200° C. only the potassium bromide gave a reaction.

(To be continued).

THE ACTION OF CYANIDE OF POTASSIUM ON GOLD AND SOME OTHER METALS AND MINERALS.*

By G. A. GOYDER, Adelaide, S.A.

(Continued from p. 263).

Lead.

SEPTEMBER 9, 1892—A piece of assay test lead weighing 1·8219 grms. placed with 6 per cent KCyAq in an inverted test-tube.

September 22, 1892—No gas given off, a slight precipitate like ferric hydrate in tube. Removed lead from the tube, washed with water, gently rubbing off deposit by the finger, rinsed in water and alcohol, warmed gently, and weighed, 1·8202 grms. showing a loss of 0·0017. Replaced lead in dish with solution but without tube, and covered with watch-glass.

October 27, 1892—Lead removed from solution and gently washed and rubbed as before; the deposit on it was white and proved to be carbonate of lead; weighed 1·8120 grms., showing a further loss by solution of the lead of 0·0082 grm.

Bismuth.

September 19, 1892—A piece of bismuth placed with 6 per cent KCyAq in an inverted test-tube.

September 30, 1892—No gas given off, no deposit in tube.

October 27, 1892—Same as last date. Bismuth taken out, washed, dried, warmed, and weighed = 0·9363 grm., replaced in solution without test-tube and loosely covered.

November 26, 1892—Bismuth taken out, washed, warmed, and weighed = 0·9355 grm., dissolved 0·0008, returned to solution.

January 10, 1893—Bismuth taken out, washed, &c., and weighed = 0·9309 grm., dissolved 0·0046 grm. The bismuth had a slight coating, probably of carbonate, white and firmly adherent. The solution was filtered, acidified with hydrochloric acid and sulphuretted hydrogen water (H_2SAq) added; this yielded a decided dark precipitate of sulphide of bismuth, showing the probable presence of a double cyanide of bismuth and potassium in the solution.

Cadmium.

September 19, 1892—A piece of cadmium weighing 6·5341 grms., but of small surface, was placed with 6 per cent KCyAq in an inverted tube.

September 30, 1892—No gas given off; tube contained a slight deposit like ferric hydrate; solution dark yellow.

October 27, 1892—Same as last date. Cadmium taken out, washed, dried, warmed, and weighed, 6·3787 grms., dissolved 0·1377; replaced in solution without tube and loosely covered.

January 10, 1893—Solution had unfortunately dried up, but the cadmium was found to be coated with a hard white scale. Water added, well stirred, and filtered; HCl and H_2SAq added to the filtrate caused a bulky yellow precipitate of sulphide of cadmium after a short time.

The white deposit insoluble in water was proved to consist of cadmium carbonate.

Part of the cadmium had therefore probably been dissolved as a double cyanide with potassium.

Arsenic.

September 19, 1892—A piece of metallic arsenic of small surface, weighing 0·4886 grm., placed with 6 per cent KCyAq in an inverted test-tube; it gave off a few minute bubbles of gas at once, but these were again absorbed by the solution, and had probably been entangled in the interstices of the metal.

September 30, 1892—No gas in tube; tube contained a slight deposit like ferric hydrate; solution rather dark yellow.

October 27, 1892—Same as last date. Arsenic taken out, washed in water and alcohol, warmed, and weighed, 0·4770, dissolved 0·0116; replaced in solution without tube and loosely covered.

November 26, 1892—Arsenic washed and weighed as before = 0·4702, dissolved since last date 0·0068 grm.; replaced in solution as before.

January 10, 1893—Arsenic washed and weighed as before, showed a further solution of 0·0006 grm., the cyanide appearing to be all decomposed by the long exposure to the air, as the solution no longer had any smell of hydrocyanic acid. The solution filtered, acidified with HCl and H_2SAq added, produced a copious yellow precipitate of sulphide of arsenic, showing that the arsenic had been dissolved, probably as the double cyanide of arsenic and potash.

Antimony.

November 3, 1892—Some metallic antimony melted and partly sublimed in a combustion tube, a current of coal-gas being passed through the tube during the heating, and the tube when cool filled with 6 per cent KCyAq and stoppered at top with an india-rubber cap.

March 10, 1892—No gas given off; solution rather dark. Solution taken from tube and filtered, acidified with HCl and H_2SAq added and warmed, produced a slight but decided orange precipitate of sulphide of antimony, indicating the probable presence in the solution of the double cyanide of antimony and potassium.

Tin.

October 28, 1892—The tin was prepared by reducing some almost pure cassiterite by fusion with cyanide of potassium, rolling out to foil, and polishing with clean sand. 2·1324 grms. was placed with 6 per cent KCyAq in an inverted test-tube.

January 10, 1893—No gas given off, tin removed, washed in water and alcohol, warmed, and weighed 2·1284 grms.; dissolved 0·0042 grm. The tin appeared slightly roughened at the bottom nearest the supply of outside air. The solution acidified by HCl and H_2SAq added gave a yellow precipitate of sulphide of tin, showing that a double cyanide of tin and potassium had probably been formed in the solution.

Mercury.

November 10, 1892—A little mercury put in a basin and covered with an inverted test-tube filled with 6 per cent KCyAq. The solution was afterwards noticed to become very dark coloured, and no gas had been given off, but the basin was accidentally tilted, and the experiment will require to be repeated. The mercury was evidently dissolved to a considerable extent, considering the small surface exposed.

The metals lead, bismuth, antimony, arsenic, tin, cadmium, and mercury appear to be acted on by cyanide of potassium, like silver and gold, the action in some cases being very slow, but no hydrogen is given off, and oxygen is absorbed. One of the great difficulties encountered in this research was that of eliminating all oxygen, and although several devices were tried, such as exhausting the air from the solutions by a mercury pump, there always appeared to be some residual oxygen left; probably the presence of a little cyanate in the solution would account for at least part of this active oxygen.

Further experiments will be made to prepare the double cyanides of these metals with potassium in a crystalline form, especially those of arsenic, antimony, bismuth, and tin, as none of those are mentioned as having been yet

* From the *Transactions of the Australasian Institute of Mining Engineers*, vol. i. Meeting held in April, 1893.

isolated in "Watts' Dictionary of Chemistry," last and previous edition; but as the action is so slow and the cyanide of potassium decomposes so readily when exposed for long intervals to the air, it will be necessary to prepare the metals in a very finely divided state, probably by the reduction of an organic salt in a glass tube and agitation with the KCyAq.

The deposit resembling ferric hydrate produced in several cases has not yet been further examined.

Magnesium.

September 23, 1892—A piece of polished magnesium ribbon weighing 0·1110 grm. placed with 6 per cent KCyAq in an inverted test-tube, gas was at once evolved rather quickly and continuously.

September 24, 1892—Evolution of gas almost imperceptible, only about 5-8th inch collected in tube; magnesium bright, no precipitate. A fresh piece of magnesium introduced when the evolution of gas occurred in the same manner as before. No further evolution of gas took place after it had stood a day, although the experiment was watched for some time.

A piece of the same magnesium ribbon was polished and placed in an inverted test-tube with dilute caustic potash solution, and behaved in the same manner as with the KCyAq solution. The experiment was repeated with polished magnesium ribbon and distilled water, and as the gas was evolved as copiously as before, it can only be ascribed to the presence of an alkaline metal, probably sodium, in the magnesium. This experiment will therefore be repeated when a sample of magnesium can be procured free from an alkaline metal.

The other metals experimented with appear to have a more energetic action, as will be seen from what follows.

Zinc.

A small sheet of commercial sheet zinc was placed with 6 per cent KCyAq in an inverted test-tube, and began to give off gas at once; the evolution of gas was continuous until the tube was full of gas and the solution depressed below the zinc. A piece of the purest zinc obtainable was tried with the same result.

Copper.

A bottle of 6 per cent KCyAq was exhausted for three days by means of a Töpler mercury pump, a piece of electrolytic copper foil weighing 5·2037 grms. put in the solution, and a bottle of boiled water inverted over the solution, so that any gas given off could be collected, the two bottles being so adjusted as to exclude the entrance of air (Fig. 1). This apparatus was set on a closed water-bath, and left till 100 c.c. of gas had been collected. The copper was then removed, washed, and weighed 4·6201, so that 0·5836 grm. had been dissolved. Gas collected 100 c.c. at 11° C., bar 769·75 = 0·00861 grm. hydrogen. According to theory the equation—

$$Cu_2 + 4KCy + 2H_2O = Cu_2Cy_2 + 2KCy + 2KOH + H_2$$

requires 0·00923 grm. of hydrogen for 0·5836 grm. of copper dissolved, the deficiency being doubtless due to a little cyanate of potash* contained in the cyanide solution, and the gas being slightly soluble in the solution. A fresh piece of the same copper, weighing 2·2222 grms., was placed in the 6 per cent KCyAq, with the gas collecting bottle arranged as before, but the solution was not heated, when 102 c.c. of gas had been collected. The copper was removed, washed, &c., and weighed 1·6624 grms., dissolved 0·5598; gas collected 102 c.c. at 18° C., bar 757·7 mil., which is equal to 0·00837 grm. hydrogen, theory as above requiring 0·00885.

Part of the gas produced in the last experiment was transferred to a graduated gas burette and found to measure 8·7 c.c.; the burette was attached by a capillary tube to a U-tube containing palladium black through which air had been passed till no more oxygen was absorbed; the other end of the U-tube was attached by a capillary tube to a simple absorption pipette filled with water, and the gas from the burette drawn over into the U-tube, where it was immediately absorbed by the palladium black, leaving a residue of only 0·04 c.c. gas. Ten c.c. of air was then introduced into the burette and passed three times over the palladium black, and the residual gas returned to the burette and measured 8 c.c., showing that all the oxygen had been absorbed from the air to oxidise the hydrogen previously absorbed by the palladium black, and proving without doubt that the gas given off by the action of KCyAq on copper was hydrogen.

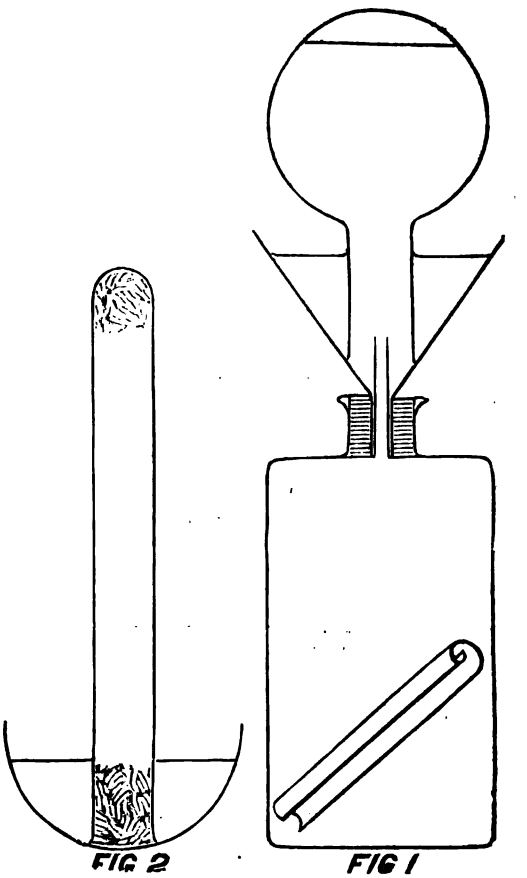

FIG 2 FIG 1

Messrs. Butters and Clennell (*loc. cit.*) in commenting on the fact that in the precipitation of the gold from the cyanide solution more zinc is required than would be necessary to complete the reaction—

$$2KAuCy_2 + Zn = K_2ZnCy_4 + 2Au,$$

appear to attribute this greater quantity of zinc required to the action of the gold-zinc couple formed by the precipitation of the gold on the zinc, which couple enables the zinc to decompose the KCyAq with the formation of caustic potash and hydrogen, &c. From the experiments given above, however, on the action of zinc, and more especially of pure copper on the KCyAq, it is at once evident that the excess of zinc would still be necessary if the formation of the copper-gold couple were avoided, and that the quantity of zinc required in excess of the gold present would be nearly proportional to the excess of free cyanide

* R. C. Maclaurin has, since the above was written, shown (*Journ. Chem. Soc.*, 1893, p. 724) that cyanate of potash does not assist the reaction, at least as far as gold is concerned.

of potassium in the solution, according to the equation—

$$2KAuCy_2+X(KCy+H_2O)+Zn=K_2ZnCy_4+2Au+ + \frac{XKOH+H}{2} + \frac{XK_2ZnCy_4}{2}.$$

It is probable that the formation of the gold-zinc couple hastens the precipitation of the gold; indeed, MacArthur-Forrest states (*loc. cit.*) that the precipitation is quicker and more complete when the zinc has a coating of gold.

From the foregoing experiments on zinc and copper it should be noted that, in using the zinc for precipitating the gold from the solution, should it be intended to use the same solution again, after adding more KCy, the solution should not remain longer in contact with the zinc than is necessary for the precipitation of the bulk of the gold, as it continually loses strength during the contact.

Only one experiment is to hand showing the quantity of cyanide left available after the solution has passed the zinc, and this was on a small experimental plant. Messrs. Graham Young and Watson Smith, in an article on "The Cyanide Process of Gold Extraction," *Journ. Chem. Trade*, 1891, 95, state:—

"With regard to the zinc treatment and cyanide left in the spent liquors, these on evaporation lost much cyanogen, but still left a residue which contained 18 per cent on the total weight of the 70 per cent cyanide taken. These liquors could hence be used again with further replenishments with cyanide."

The analysis of the liquors from a large plant in full working would be of interest on this point.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 17th, 1894.

Dr. Armstrong, President, in the Chair.

Professor D. Mendeleef, of St. Petersburg, Foreign Member of the Society, being present signed the Roll of Fellows.

Certificates were read for the first time in favour of Messrs. Cecil Cooke Duncan, Royal Agricultural College, Cirencester; Bhirkaji Edalji Ghasvala, Tardes, Bombay; Donald Gordon Forbes, Shillingstone, near Blandford, Dorset; Richard S. Ladell, 11, Lower Grosvenor Place, S.W.

Of the following papers those marked * were read:—

*17. "*The Influence of Moisture on Chemical Action.*" By H. Brereton Baker, M.A.

Since the publication of a note in the *Proc. Chem. Soc.* (May 4th, 1893) further investigations of the actions there mentioned have been made. Sulphur trioxide does not combine with highly purified lime; but a trace of moisture brings about vivid incandescence. Dry copper oxide is also without action on sulphur trioxide. Purified and dried lime does not decompose dried ammonium chloride, which may be sublimed from the mixture without evolving any ammonia. Purified and dried nitric oxide gives no brown fumes with dried oxygen, but a trace of moist air causes them to appear at once. A mixture of purified and dried hydrogen and chlorine can be exposed to daylight for four days without more than three-fourths of the gases combining. Ammonium chloride, heated in a vacuum in a soft glass tube, leaves a residue of ammonia gas; but when dried and heated in a hard glass tube, no gaseous residue is obtained. This led to the investigation of the vapour density of dry ammonium chloride, which was shown to be normal, 28·7 being the mean result of six experiments. With regard to the theory of the subject, the author believes that an electro-chemical hypothesis is applicable. Separation of dried ammonia and hydrogen chloride gases takes place when plates with opposite electrical charges are introduced into the mixture though the action cannot be electrolytic, since discharge is, under the circumstances, impossible. Similar separation was noticed with air and with a mixture of dried hydrogen and oxygen. Electric discharge, when not of high tension, will not pass in dried gases; but the high tension discharge does pass, and renders it possible for the low-tension discharge to pass afterwards. With regard to the influence of moisture, it appears that what holds for chemical combination holds also for electrical discharge, and that there is great significance in the apparent similarity in the two cases.

Discussion.

The President spoke of Mr. Baker's results as of great value and as calculated to convince all of the important influence exercised by moisture in promoting very many chemical changes; he had long been satisfied that the presence of an electrolyte was essential to every chemical change, and that water was of service because it gave rise to an electrolyte. It was now important to ascertain whether other substances besides water could condition the formation of electrolytes and thus co-operate in producing change, and to determine what their nature was; probably water was one of a very few substances able to act in this manner, if indeed it were not the only one. In the case of hydrogen and chlorine, there was reason to think, as Mr. Shenstone had indicated, that some substance other than water was also essential to the occurrence of change.

He was glad to hear Mr. Shenstone say that he was not yet satisfied that pure oxygen can be ozonised; his statement that more ozone was obtained from dried oxygen might be regarded as evidence that water influenced its formation; the amount of ozone finally obtained depended on the amount destroyed as well as on the amount originally formed, and if both its formation and destruction were influenced by moisture, it might well be that one action was more directly influenced than the other when but very little moisture was present. If the destruction took place the less rapidly the less water present, the amount finally obtained would be the greater the more carefully the oxygen was dried.

Regarding the decomposition of ammonium chloride by heat, although moisture would promote its decomposition, the absence of moisture would not have the effect of making it a stable substance at all temperatures; it might be expected that, if dry, it would *decompose* when heated sufficiently, but would not *dissociate*; in other words, there would be no re-formation of ammonium chloride under such conditions.

Mr. Shenstone was glad to find that Mr. Baker's results had confirmed his own earlier experiments on the production of ozone from oxygen and on the action of ozone on mercury. At the same time he was not yet himself convinced that really dry oxygen would ozonise, and he was at present studying the influence of moisture on the formation of ozone from oxygen quantitatively. He expected the character of the curve obtained would settle the question.

He could also, from the results of many experiments, confirm Mr. Baker's statements as to the persistent activity of highly dried chlorine towards certain substances. Its action on mercury, for example, was often apparently independent of dryness. In fact, the results obtained pointed to the presence of some other substance than water, as being able to influence the action of these two substances. This had led him to search for a more satisfactory source of chlorine.

*18. *New Volatile Compounds of Lead Sulphide.*" By J. B. Hannay.

Early experimenters, notably Pattinson, Regnault, and Jordan, have noticed the volatilisation of lead sulphide in

water vapour and its subsequent crystallisation, but their results in other respects seem to be irreconcilable.

An investigation showed that all the phenomena described are easily understood, on the supposition that both water and sulphur dioxide combine at high temperatures with lead sulphide, forming gaseous compounds. When difference of temperature is taken into account, it is found that water vapour reacts with lead sulphide in the following manner:—

1. About 750° .. .. $PbS+H_2O=PbO\cdot H_2S$
2. „ 900° .. .. $2PbO+2PbS=3Pb+PbS_2O_2$
3. „ 1400° .. .. $PbS+H_2O=PbS\cdot H_2O$

Neither of the first two changes is complete, but in each the sulphide is decomposed. In the third reaction, however, there is no decomposition, and the sulphide is redeposited on cooling. Reasons are adduced for the conclusion that a definite molecular compound $PbS\cdot H_2O$ exists.

Similar indirect evidence is given to demonstrate the existence of the compound PbS,SO_2, or PbS_2O_2. Both these compounds are colourless gases at a red heat, but when the temperature falls decomposition occurs. This remarkable fact is explained by the observation that the oxygen of sulphur dioxide and of water displaces the sulphur of the lead sulphide temperatures near 800°, whilst at higher temperatures, such as 1400°, both sulphur dioxide and water combine with lead sulphide, and redeposit it on cooling.

Discussion.

After remarking that the subject brought forward by Mr. Hannay evidently gave abundant opportunity for discussion, the President said that, assuming that a volatile compound of the formula $PbS\cdot SO_2$ existed at high temperatures, the properties assigned to it by Mr. Hannay were not of the unique character he appeared to suggest; numerous cases were recorded of compounds which underwent change as the temperature fell, but probably this was due, not to their intrinsic instability, but to the tendency of such molecules to interact among themselves. At high temperatures lead sulphide might consist of simple (di-atomic) molecules capable of combining with those of other substances, while at lower temperatures such molecules might associate, forming galena, which probably was a polymeride of the compound PbS. The extrusion of oxygen from molten silver and of carbon dioxide on freezing soda water, might be regarded as cases comparable with those brought forward by Mr. Hannay, and such an explanation would apply to them.

Professor Roberts-Austen said that the metallurgy of lead presented many peculiarities. One of these is the necessity of condensing volatile products of the reactions, which had led smelters of lead ores to construct condensing flues which might reach a mile in length. The author of the paper would, therefore, be doing good service if he added to our knowledge of the condensible products formed during lead smelting. But the question arose, Had the author of the paper established the fact that water vapour and sulphurous anhydride really carry away sulphide of lead in molecular proportions? There are, as the President had said, many instances of compounds which are stable at a high, and unstable at a low, temperature, and this is a point in Mr. Hannay's favour, but the extreme solvent action of litharge itself must not be forgotten, and litharge, moreover, absorbs oxygen when fluid, and evolves it again on solidification; the effects observed by Mr. Hannay may, therefore be in some way connected with the solvent action of litharge. It appeared to the speaker that the evidence given by the author of the paper as to the existence of volatile compounds of sulphide of lead and sulphurous anhydride was of the most slender description. If it were possible to obtain evidence as to the vapour density of the volatile products, that would, of course, settle the question, but the author's main evidence appeared to rest on observations made by looking along a red-hot tube, and recording whether certain vapours did or did not form as the temperature is varied. It appeared that Mr. Hannay had not even satisfied himself that when the alleged compounds are cooled down and become unstable they yield their constituents in exactly the proportions demanded by his theory. The evidence afforded by the composition of the "lead fume" which accumulates in the condensing flues is not without importance, but, upon this point, Mr. Gowland would state the results of his experience. Professor Austen gathered that Mr. Hannay objected to the accepted equation $PbSO_4+PbS=2SO_2+2Pb$, on the ground of the comparative infusibility of the sulphide and sulphate of lead, but it must be remembered that many substances interacted by "fritting" at temperatures well below their melting-point. Percy's statement as to the separation of lead, under the conditions represented by the equation, was very definite, and Dr. Percy was very careful, and did not make such statements except on the clearest experimental evidence. The action is, however, an endothermic one, and it would certainly be well to re-examine the conditions with great care. Assuming that the accuracy of the accepted equation—

$$PbS+2PbO=3Pb+SO_2$$

(which is less endothermic than the first) can be maintained, surely the fact that lead is the result of the reaction points to the instability at a red heat of Mr. Hannay's compound of sulphide and oxide of lead. Lead sulphide and lead oxide had long been known to be volatile at moderate furnace temperatures, and chemists must certainly have more evidence than that now presented to them before they could accept Mr. Hannay's conclusions.

Mr. Gowland did not think that Mr. Hannay had given us sufficient proof that a substance of the formula PbS_2O_2 exists; he does not appear to have isolated it, neither has he shown adequate grounds for regarding it as a product of the smelting of lead sulphide.

The conditions of Mr. Hannay's experiment are not similar to those which occur in the reverberatory furnace in actually smelting lead sulphide. It is generally admitted that the two compounds formed in this operation, viz., lead oxide and sulphate, are volatile in a current of air (see Percy's "Metallurgy of Lead," pp. 15—42), and that these substances are the chief constituents of the volatile products condensed in the flues of the smelting furnace.

Again, if the lead lost by volatilisation is volatilised as PbS_2O_2, the volatile products which are condensed in the flues as "lead fume" should consist mainly of it, or of the product of its decomposition—lead sulphide. This is, however, not borne out by analysis of "lead fume." In a typical specimen, analysed in Percy's laboratory, the lead, sulphur, and oxygen existed in the following proportions:—Pb, 68·47 per cent; S, 11·25 per cent; O, 20·28 per cent; whereas, if the fume had consisted of PbS_2O_2, or its products of decomposition, these proportions should have been Pb, 68·32; S, 21·12; O, 10·56, or Pb, 86·61; S, 13·39, or some intermediate proportion.

Until further proof of the existence of PbS_2O_2 has been obtained, we have not sufficient grounds for setting aside the old explanation of the chemistry of lead smelting as set forth by Percy and other distinguished metallurgists.

Mr. A. G. Bloxam stated that some recent experiments at the Goldsmiths' Institute had shown that galena could be volatilised in both hydrogen and nitrogen. The mineral was heated in a porcelain tube situated in a furnace very similar to that depicted by Mr. Hannay, so that it seemed fair to conclude that the temperature attained was approximately the same as that at which Mr. Hannay worked. The gases were purified by passage through (1) silver nitrate solution, (2) alkaline permanganate solution, (3) red-hot copper, and (4) columns of quicklime and of phosphorus pentoxide. The text-book statement that galena could be volatilised in hydrogen, forming some hydrogen sulphide, was confirmed. In the case of heating

in nitrogen, large crystals of galena were afterwards found in the cooler part of the tube, and a sublimation of sulphur was noted.

Mr. Hannay said, in reply to Professor Roberts-Austen, that the discussion showed how much this difficult subject required to be considered before a true appreciation of the evidence could be arrived at. The last experimental work on the subject was done in 1830. As to the evidence establishing the existence of the compounds being insufficient, a study of the paper would show that all the reactions are quite definite, and that the analysed CO agree with the composition given.

The paper did not deal with lead smelting, and some of the diagrams exhibited merely showed the part played by the new volatile compound in certain reactions.

In reply to Mr. Gowland, Mr. Hannay pointed out that lead sulphate is not volatile at the temperature of the smelting furnace, and that the flue dust, to which reference was made, was simply the product of oxidation (or partial oxidation) of the volatile compound PbS_2O_2, which is formed in the furnace. As PbS_2O_2 decomposes on cooling, it is useless to look for it in the flue-dust; we only find its products of decomposition. It would be very difficult to determine its vapour density.

The speakers in the discussion seemed inclined to adhere to the old equation $PbS+O_2=Pb+SO_2$; but this equation seemed to be only hypothetical, and unsupported by experimental proof. As the subject evidently required further elucidation, Mr. Hannay promised to prepare a paper dealing minutely with this part of the metallurgy of lead.

In reply to Mr. Bloxam, Mr. Hannay stated that it is quite true that minute quantities of lead sulphide are volatilised by all gases, but the action of water and sulphur dioxide brought about a sudden and copious evolution of fumes, and the composition of these fumes could be represented by a definite molecular proportion.

19. "*Notes on the Cupellation of Bismuth-silver Alloys.*" By Ernest A. Smith, Assoc. R.S.M.—(See p. 255).

20. "*Azo-p-cresol Derivatives.*" By R. Meldola, F.R.S., and F. Southerden.

The reduction of the acetyl- derivatives of oxyazo-compounds of the ortho-series has been shown to give ambiguous results so far as concerns the question of the constitution of these compounds (Meldola, Hawkins, and Burls, *Trans*, 1893, 923). An attempt was therefore made to solve the problem by the more direct method of decomposing the acetyl-derivatives by means of nitric acid or bromine. In the case of the alkyl-derivatives of benzeneazo-β-naphthol, the nitric acid method gave a definite indication that the alkyl group is hydroxylic and not amidic (Meldola and Morgan, *Trans.*, 1889, 608). In the case of the acetyl-derivatives of benzeneazo-β-naphthol, nitric acid appears to act simply as a nitrating agent (*ibid.*, 609). We have applied the same method to some ortho-azo-derivatives of *p*-cresol, and the results are submitted in the present note.

Paratolueneazo-*p*-cresol was prepared and acetylated (Nölting and Cohn, *Ber.*, 1884, 354). The acetyl-derivative, on reduction with zinc dust on acetic acid, gave, as the only definite product, acetoparatoluide. Acetamido-*p*-cresol may have been formed, but lost by oxidation during the treatment necessary for the isolation of the acetoparatoluide. Resinous colouring-matters are formed during the evaporation of the solution by the oxidation of some unstable compound resulting from the reduction. The original compound (paratolueneazo-*p*-cresyl acetate) is brominated by the action of bromine, but the azo-group is not split off and no separation of the molecule takes place, as, *e.g.*, in the case of benzeneazo-β-naphthylamine.

Benzeneazo-*p*-cresol was acetylated (Nölting and Cohn, *Ber.*, 1884, 353) and the product, dissolved in glacial acetic acid, was allowed to stand for two or three days with an excess of bromine. A crystalline substance slowly formed, which, after repeated crystallisation from glacial acetic acid and finally from alcohol, formed golden brown needles with a silky lustre, melting at 168°. Analysis proved the compound to be a dibromo-derivative of benzeneazo-*p*-cresol. Calculated for $C_{13}H_{10}Br_2N_2O$; Br, 43·24 per cent, N, 7·57 per cent. Found, Br, 43·50 and N, 7·64 per cent.

The acetyl-group thus splits off under the influence of bromine; the azo-compound simply becomes brominated, and, as no separation of the molecule takes place, the products were not further investigated.

Parachlorobenzeneazo-*p*-cresol was prepared in the usual way by mixing a solution of diazotised parachloraniline with an alkaline solution of paracresol. The product, when purified by crystallisation from alcohol and benzene in succession, forms flat golden orange needles, melting at 155°. The compound appears to exist also in another crystalline form, as the rapid evaporation of the benzene solution gives rise to a deposit of small, opaque, ochreous needles, having the same melting-point. The purity of the compound was ascertained by analysis. Calculated for—

(*p*) $Cl{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(CH_3){\cdot}OH$ [$N_2:CH_3:OH=6:4:1$]; Cl, 14·43 and N, 11·36 per cent. Found, Cl, 14·46 and N, 11·45 per cent.

The acetyl-derivative was prepared by boiling the foregoing compound with excess of acetic anhydride for about twenty hours. After crystallisation from alcohol, it forms orange needles, melting at 120°.

Calculated, Cl, 12·31 and N, 9·61 per cent. Found, Cl, 12·46 and N, 9·78 per cent.

As bromine had acted on these compounds merely as a brominating agent, the substance was acted upon by nitric acid of various strengths and under various conditions. Nothing of the nature of a nitrated aniline, acetanilide, amido- or acetamido-cresol was, however, obtained. Nitric acid appears to nitrate the azo-compound as a whole, forming a yellow uncrystallisable product, apparently of the same nature as that resulting from the nitration of benzeneazo-β-naphthyl acetate (*Trans.*, 1889, 609).

21. "*Effect of Heat on Iodates and Bromates.*" By Ernest H. Cook, D.Sc.

This paper is the first instalment of an account of the experiments made upon the effect of heat upon iodates and bromates. It deals with potassic iodate and bromate. Details are first given of the methods of purification of the reagents used. Exceptional difficulties were experienced with potassium iodide, and the ordinary methods of purification adopted were shown not to yield a sufficiently pure product. The paper of Robineau and Rollin (*Journ. Pharm.*, [5], xxvi., 485—490), in which they state that "all acids, even carbonic anhydride, in presence of air and moisture, decompose potassic iodide," is quoted, and a series of experiments to test the truth of this statement are detailed. The results obtained show that the statement is only partly true.

The methods adopted for the analysis of the oxy-salts are then given. These were of three kinds:—(1) Digestion with potassic iodide and hydrochloric acid; (2) reduction by sulphurous acid; and (3) reduction by the copper-zinc couple. These methods are compared, and the precautions necessary for success are stated. In the first it is shown that accurate results can only be obtained when a blank experiment with potassium iodide and hydrogen chloride is carried on side by side with the principal one.

Potassic iodate is difficult to purify; repeated crystallisations from water fails to give a reliable product. The method adopted was, therefore, to crystallise from water once or twice, then to precipitate the solution by means of alcohol, collect the precipitate, and re-crystallise from water. The first effect of heat on the iodate is to cause the substance to become brown. This brown substance has the same composition as the original iodate, and it is formed without any alteration taking place in weight. When the

heating of the iodate is continued up to the time of its ceasing to lose weight, the following changes are observed:—The brown substance fuses and becomes a colourless liquid, during the fusion, iodine is evolved; after continued and regulated heating, the liquid becomes a white solid, and when thoroughly solid ceases to lose weight; the residue is potassium iodide.

The next point studied was the partial decomposition of the iodate. The salt was heated for varying periods, the amount of loss ascertained, and the residue analysed. The results showed that no other oxy-compounds were formed at any stage of the process.

Potassium bromate was next experimented with, the total decomposition of the salt by heat as well as the partial decomposition being studied. No change of colour occurs with the bromate, but the salt decrepitates at about 180° C. During the decrepitation bromine is evolved, but at no other stage of the process. The salt fuses to a colourless liquid, from which oxygen is steadily evolved; the residue consists of potassium bromide.

The partial decomposition indicated the presence of breaks in the rate of evolution of the oxygen; these were shown to be due to the mode of heating, and not to definite chemical reactions. The residue consists of a mixture of bromate and bromide.

These experiments having failed to produce any oxy-compounds, it was thought that these compounds might be formed if the heating were effected under reduced pressure; but at a pressure of 30 m.m. the results were precisely the same as under normal conditions.

Finally, in order to discover at what stage the chlorine known to be evolved when chlorate is heated is produced, experiments were made with that substance. It was found that the chlorine was evolved just at the same period as the iodine from the iodate, viz., during the melting of the salt. The amount formed is 0·03 per cent.

It would, therefore, appear that the halogen is liberated early, but that it is not actually set free until the structure of the salt is broken down—in the case of the iodate by fusion, and in that of the bromate by decrepitation.

PHYSICAL SOCIETY.

Ordinary Meeting, May 25th, 1894.

Prof. A. W. RÜCKER, M.A., F.R.S., President, in the Chair.

PROF. W. RAMSAY, F.R.S., read a paper on "*The Passage of Hydrogen through a Palladium Septum, and the Pressure which it Produces.*"

After referring to the analogy between osmotic pressure of solutions and the behaviour of hydrogen and palladium, the author described the apparatus he had used in his experiments, and showed it in operation.

A vertical platinum tube provided with a palladium cap is enclosed within a glass vessel through which hydrogen or other gases may be passed, and outside the glass vessel is a vapour jacket by means of which a constant temperature can be maintained. The lower end of the platinum tube communicates through a graduated capillary tube with an adjustable manometer, which enables the volume of the enclosed gas to be kept constant. Great precautions were taken for ensuring purity and dryness of the gases used.

After filling the palladium and platinum tube with dry nitrogen at atmospheric pressure and the desired temperature, hydrogen was passed through the glass vessel. Some of the hydrogen permeated the palladium walls, thus increasing the pressure inside. After some time (usually an hour or so) the pressure attained a steady value, and the total increase was then observed. Experiments were made with air, nitrogen, nitric oxide, nitrous oxide, carbon dioxide, carbon monoxide, and cyanogen in the palladium tube, and in some cases the hydrogen was diluted with nitrogen. In all cases the maximum pressure of the hydrogen within the tube was less than that of the hydrogen outside the tube, as will be seen from the accompanying Table, which shows the ratio of these pressures under various conditions.

After the palladium had been used once or twice it became coated with mercury (vapourised from the manometer) and lost its permeable properties). It was found necessary to heat the tube to remove the mercury, and then dissolve off the oxide of palladium thus produced after each experiment. The permeable nature of palladium was found to depend greatly on the temperature, for at 232° C. the passage of hydrogen was so slow that the internal pressure was still rising after ten days; at 330° the passage was very rapid. An attempt to use the apparatus for giving a continuous indication of the amount of hydrogen in coal-gas failed because the palladium did not retain its activity sufficiently long. Other experiments showed that nickel is impervious to carbon monoxide.

In the latter portion of the paper the author discusses the various "so-called" explanations which have been given of the phenomena, but finds none satisfactory. Experiments on the absorption of gases by platinum and other metals are in progress with a view to the further elucidation of the subject.

Mr. MOND thought the fact that rise of temperature accelerates diffusion tended to confirm Graham's view that the gases pass through openings in the solid, for increase of temperature would widen any pores which might exist in the metal.

The PRESIDENT enquired whether the author's argument against the possibility of palladium hydride condensing in the pores of the metal, because of its being unstable at the temperature employed, would be affected by the fact of water being capable of existing in contact with glass at temperatures much above boiling-point.

In reply Prof. RAMSAY said the President's suggestion might be true, but if so another condition must be fulfilled, viz., that the hydrogen molecules must be split up into the atomic or *nascent* state.

A paper on "*The Relations of Pressure, Volume, and Temperature of Rarefied Gases,*" by Prof. W. RAMSAY, F.R.S., and E. C. C. BALY, was read by the latter.

In the first part of the paper a historical summary of previous researches on the subject is given and the chief sources of error pointed out. The method employed by the authors was to have two McLeod gauges connected with a pump, and arranged so that both could be trapped under exactly the same pressures. One of the gauges was surrounded by a vapour jacket at about 130° C., whilst the other was cold at about 13° C. After both were trapped the hot gauge was allowed to cool and the readings of both taken. From these observations the coefficient of expansion of the gas used could be calculated.

Gas originally inside tube.	Gas passed outside tube.	Temperature.	Ratio: $\frac{\text{Internal hydrogen pressure.}}{\text{External hydrogen pressure.}}$
Nitrogen.	Hydrogen.	280° C.	0·9053
,,	,,	335° C.	0·8984
,,	Hydrogen 50 per cent (rest nitrogen).	335° C.	0·9362
,,	,, 25 ,, ,,	335° C.	0·9344
Carbon dioxide.	Hydrogen.	280° C.	0·9621
Carbon monoxide.	,,	280° C.	0·9545
Cyanogen.	,,	280° C.	0·9693

The experiments also served as tests of the reliability of the McLeod gauge under different conditions. For air and carbon dioxide the gauges proved quite unreliable, whilst for hydrogen they were fairly satisfactory. With carbon dioxide the surface condensation was so large as to make the observations worthless, but hydrogen suffered no condensation between pressures of 650 m.m. and 0·000076 m.m. Great difficulty was experienced in filling the gauges with pure hydrogen, but when accomplished the expansion was proved to be normal ($\frac{1}{273}$) down to 0·4 m.m. pressure, and diminished to $\frac{1}{300}$ at 0·07 m.m. Oxygen, however, gave a coefficient of $\frac{1}{281}$ at 5 m.m. pressure, $\frac{1}{350}$ at 2·5 m.m. and $\frac{1}{282}$ at 1·4 m.m. At 0·7 m.m. its behaviour was most erratic, there being as much as 15 times the amount of gas trapped in the gauge at one time as at another. This confirms C. Bohr's observations on the anomalous behaviour of oxygen about this pressure. For nitrogen the values of the coefficients found were $\frac{1}{300}$ at 5 m.m., $\frac{1}{273}$ at 1·1 m.m., and $\frac{1}{273}$ at 0·6 m·m. At small pressures the elasticities of hydrogen, nitrogen, carbon dioxide, and air increase with decrease of pressure, but in oxygen the reverse holds. Examining the consequences of this increase of elasticity, in the light of the kinetic theory of gases, the authors point out that it means an increase of internal energy, and suggest that this may be the cause of phosphorescence in high vacua.

The PRESIDENT announced that the discussion on the last paper would be taken at the next meeting after proofs had been distributed to members.

NOTICES OF BOOKS.

Law and Theory in Chemistry: a Companion Book for Students. By DOUGLAS CARNEGIE, M.A., sometime Scholar and Demonstrator in Chemistry of Gonville and Caius Colleges, Cambridge. London and New York: Longmans, Green, and Co. 1894.

THIS work, as appears from the sub-title "Companion Book," consists, as the preface informs us, of seven short and independent essays on the subjects of which they severally treat. The author does not seek to furnish a text-book in addition to the many which already exist, but he discusses ably and thoughtfully subjects which, though essential to a full understanding of the science, are inadequately treated in the current elementary text-books, or are altogether crowded out. We might almost pronounce it a compact history and philosophy of chemical science. He scarcely lays sufficient emphasis on the fact that alchemy was not the origin of chemistry, but a parasitic growth by which it was attacked in its early stages of growth. In summarising the opinions of the Greek philosophers, he makes a quotation which clearly shows the radically anti-scientific tendency of the Socratic school. Says Plato in the seventh book of his "Republic":—"If we wish to become thoroughly acquainted with astronomy, we will best let the heavenly bodies alone!"

The Iatro-chemists are spoken of as the successors to the elder alchemists. The Iatro-mathematicians, their rivals, are not mentioned, perhaps because their harmful tendency—against the possible revival of which we must be on our guard—was directed not so much towards chemistry as towards what we now call biology. Reference is made to advertisements which appeared in an eminent literary paper offering to teach, for a fee, all the secrets of the Hermetic Art in a course of nineteen lessons.

As evidence of a similarly unscientific state of mind Mr. Carnegie mentions an advertisement which appeared in *Nature* (August 17, 1893), where a sage offers to teach the quadrature of the circle for a fee of five shillings. Patents are still applied for, *and granted*, for the perpetual motion.

Mr. Carnegie, in his second chapter, devoted to the "Phlogistic Period and the Beginnings of Chemical Theory," mentions death by "spontaneous combustion," a phenomenon believed in by G. H. von Schubert, and which figured in the literature of the present century ("Bleak House," preface and Chapter XXXII.), giving rise to a lively passage of arms, in which G. H. Lewes vainly sought to convince Charles Dickens of the unreality of this imaginary phenomenon.

Boyle seems to have the honour of being the first to notice that bodies on combustion increase in weight, and Hooke, at one time assistant to Boyle, failed little of demonstrating that fire is not an element but a phenomenon arising from the agitation of particles, or, in more modern phraseology, "a mode of motion."

The career of Priestley is noticed at some length, and in a manner capable of misleading. He is styled "the English divine." A reader might be led to the erroneous conclusion that Priestley was a clergyman of the Church of England. It is added "Priestley did not allow his *Calvinistic* doctrines to usurp his whole interest and leisure." His doctrines, had he lived in Geneva under the sway of John Calvin, would have ensured his sharing the fate of Servetus. He lived and died a persistent phlogistian. When he had discovered oxygen he did not, like his predecessors Hooke and Mayow, regard it as a constituent of air, but merely as common air freed from impurities.

Though persecuted in the latter part of his life we cannot claim him as a martyr of Science. He suffered not as the discoverer of oxygen and the successful worker in pneumatic chemistry, but as the symphathiser with French Jacobinism. Had he followed the wise advice of Edward Gibbon and "stuck to his chemistry," "not a dog would have barked at him." Hence his remark on bidding farewell to his native land was founded on a mistake. If we now do honour to his memory, it is because we condone his theological and political peculiarities for the sake of his scientific researches.

Henry Cavendish is mentioned here as that "peculiarly ascetic philosopher." Like Priestley, Cavendish was unable to emancipate himself from phlogiston. He failed to grasp the conclusion necessitated by his own researches.

The fact that the great development of chemistry coincided in time with the French revolution, is somewhat misrepresented in the following sentence:—"It is remarkable that the most fearful reign of anarchy and bloodshed the modern world has known should have bequeathed to us, through Lavoisier, so unexpected a gift as a re-modelled and thoroughly scientific theory of chemistry." We must never forget that the tendencies of the revolution were distinctly anti-scientific. Besides guillotining Lavoisier, it abolished the Academy of Sciences, and declared that "the Republic had no need of *savans*."

Space does not permit us to prolong our notice of this valuable work. We can safely recommend its careful perusal to all more advanced students, who will indeed find it a useful "companion book."

Electric Light Installations. Vol. II. Apparatus. By Sir DAVID SALOMONS, Bart., M.A. Seventh Edition, Revised and Enlarged. London: Whittaker and Co. 1894.

THE volume now before us shows incontestably that its author is not a mere theorist, or, may we say, an official electrician, but a thoroughly practical man, as well able to take off his coat and run an installation as to preside at a meeting or read a scientific paper.

This grasp of detail will, we feel sure, be appreciated by those who have been through the mill themselves. Little dodges that many people would not think worth recording, or would, perhaps, jealously keep to themselves, are often—nay, invariably—as important to successful

working as a knowledge of the broad outlines of running and tending machinery. It is principally on these grounds that we congratulate Sir David Salomons on the value of his work.

The first consideration in an electrical installation is the prime motor; this may be worked by steam, gas, oil, &c., and the advantages of one or the other for particular purposes are fully considered in Chapter I.

The next chapter is devoted to Dynamos and Motors. all the principal patterns being herein described. In speaking of automatic safety devices, which have been often condemned as uncertain in their action, the author points out that even in that case they are no worse than, but possibly preferable to, a man, who sometimes forgets; but he says very truly that "the present age may be described as one in which the less a man has to do the less he is disposed to do, and the greater must be his pay." This appears to us to be an argument against the use of automatic apparatus.

After a chapter on Instruments, we come to the important subject of governors. By the word "governor" it is not to be understood the ordinary governor of an engine (steam or otherwise), but one to either maintain a constant pressure or keep up a regular current. The most simple and we think the most rapid way of working such governors is to make the electric energy itself do the work. Several types of such governors are described, each adapted for special conditions of working.

Switches, cutouts, connectors, and such like minor apparatus, form the subjects of Chapters V. and VI.; while Chapter VII. treats of the comparatively small subject of arc-lamps. The application of these lamps is necessarily limited, while their high price is in many cases a serious drawback.

Chapter VIII. is devoted to the thousand and one practical applications of electricity. Surprising as it may seem, the general public is still very ignorant as to what can and what cannot be done by its means. As time goes on, new applications are springing up in ever-increasing numbers, and if anything like the recent rate of progress is maintained, the next generation will be far more ahead of us than we are of our predecessors of even one hundred years ago.

The book is profusely illustrated with 296 figures, which greatly assist the descriptions in the letterpress.

CORRESPONDENCE.

"THE ORGANIC COMPOUNDS OF EVERY DAY LIFE."

To the Editor of the Chemical News.

Sir,—At the risk of seeming to give too much attention to a small matter I wish to express my regret that in the notice which you gave my little book on "The Organic Compounds of Every Day Life" (Chem. News, vol. lxix., p. 180), the writer seemed to have overlooked the preface entirely. Reference to that will show that the book was written to meet certain "special needs in the instruction of students," and "to present that knowledge of organic compounds which is necessary to the most successful pursuit of agriculture, mechanic arts, and domestic economy." Under these circumstances the critic would not, I presume, deny to me as a teacher the moderate use of graphic formulæ accompanied by proper explanation of their meaning and limitations. The book is not addressed to "the outsider," but to students of chemistry in a limited course in which special attention is given to the so-called *practical* features. I believe, however, that no proper grasp of practical points can be obtained without an understanding of the fundamental chemical properties of the substances discussed; hence the book is "more technical and less readable" of necessity. The title may not be happily chosen, but it was the result of a feeling on my part that so elementary a volume could not with due modesty be called even an introduction to organic chemistry.

I set so high a value upon the book reviews of the Chemical News that I sent you the volume in the hope that, if it was deemed worthy of any notice, you would express a judgment upon my success or failure in my object, viz., to present to students the most elementary principles of organic chemistry and their relations to the facts of inorganic chemistry, as illustrated by the compounds of every-day life, together with an accurate statement of the most interesting applications of these substances to the arts and sciences, the latter feature being comparatively neglected in all the elementary text-books which have come to my notice.—I am, &c.,

J. T. Willard.

Kansas State Agricultural College,
Manhattan, Kas., May 12, 1894.

[Mr. Willard, if he meant his book for the use of students, has not been happy in that difficult matter the choice of a title. The one selected irresistibly reminds the reader of Johnston's "Chemistry of Daily Life." We imagined—perhaps not unpardonably—that Mr. Willard was seeking to produce a companion volume to Johnston's admired and successful work. For such a production which should expound the aims and results of modern synthetic chemistry to the cultured outsider there is ample room. But the author disclaims a view so sure to be inferred from his title, and tells us that he has been addressing "students of chemistry in a limited course in which special attention is given to the so-called practical features." This admission complicates the question, since elementary works on chemistry, addressed to students, have been, in Britain at least, so numerous that we fail to see their *raison d'être*. To include in one small treatise the fundamental principles of organic chemistry and their industrial applications is indeed a difficult task. We are glad to find that Mr. Willard enters no protest against our strictures on his prominent notice of the "high explosives"—those favourite agents of the Nihilist, the dynamitard, and the anarchist. If we have inadvertently hurt his feelings by our remarks we must disclaim any intentional discourtesy, and hope that on further consideration he will acquit us of any unfairness.—*Ed.* C.N.].

Absorption-spectra of Hydrobromic Solutions of Cupric Bromide.—Paul Sabatier.—The absorbent power very well marked in the alcoholic solutions of the anhydrous bromide is much greater for solutions in concentrated hydrobromic acid. For a proportion of copper below 0·5 grm. of metal per litre, the aqueous solution is nearly colourless; the alcoholic solution is of a distinctly yellowish brown colour, but still very transparent. The hydrobromic solution is almost opaque. To observe the absorption-spectrum it is necessary to operate upon hydrobromic solutions very weak in copper or upon very shallow strata of the liquid. This is a condition far from favourable to the exact determination of the coefficients of transmission. Another difficulty lies in the spontaneous change of the liquids. On observing a recent solution containing 0·150 grm. of copper dissolved in the state of cupric bromide with 780 grms. of hydrobromic acid, and seen in the thickness of 2·5 m.m., it is found that the transmission of light, very decided in the red, decreases rapidly in the yellow and the green, presents a distinct minimum in the blue about $\lambda = 503\ \mu\mu$, and then increases anew in the indigo and the violet. The colour of the whole is purple. It is found that from $\lambda = 660\ \mu\mu$ the absorption is intense. As soon as we increase the depths of the solution or its percentage of copper, we perceive merely the red rays of wave-lengths above 680 $\mu\mu$. Hence the great sensitiveness of the author's method for distinguishing traces of copper.—*C. R.*, cxviii., No. 21.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 21, May 21, 1894.

M. Laussedat was nominated a Free Academician *vice* the late General Faye.

The Industrial Section of the Society of Arts of Geneva announces that it has opened a subscription for erecting a bronze bust to Daniel Colladon in one of the Squares of the City of Geneva.

Researches on Trimethylene and Propylene, and on a New Class of Hydrogen Carbides. Dynamic Isomerism. — M. Berthelot. — Trimethylene and propylene isomeric gases of the formula C_3H_6 differ by their heat of formation from their elements, carbon (diamond) and hydrogen, as $-9{\cdot}4$ cal. for propylene and $-17{\cdot}1$ cal. for trimethylene, that is, an excess of energy of $+7{\cdot}7$ cal. in favour of the latter. We see that the transformation of methylene and of propylene into isomeric combinations gives rise to very unequal developments of heat, differing by from 8 cal. to 10 cal. The excessive energy of trimethylene compared with propylene does not exist in the parallel combinations of these two gases; it is lost in the act of combination. If we add that the formation of similar combinations liberates approximately the same quantities of heat, whether with propylene or with ethylene, it is seen that trimethylene has something quite peculiar in its constitution. It is placed outside the homologous series studied hitherto, from which it is distinguished by the exceptional energy stored up in its formation. I have already pointed out in a research executed by M. Matignon analogous relations between turpentine and its isomers, camphene and citrene, all carbides represented by $C_{10}H_{16}$. The formation heat of liquid turpentine from its elements is equal to $+4{\cdot}2$ cal., whilst that of liquid citrene reaches to $+21{\cdot}7$ cal., and that of crystalline camphene to $+27{\cdot}2$ cal., or in the liquid state about 24 cal. Turpentine, therefore, in relation to its isomers, contains an excess of energy equivalent to +18 or +20 cal. Strangely enough, this excess is lost in the parallel combination of the three substances with hydrochloric acid. Turpentine, in forming a hydrochlorate, evolves 19 to 20 cal. more than the isomeric carbides, a figure close upon the excess of energy which distinguishes it from these carbides. Hence it results that the formation-heat of the isomeric hydrochlorates from their elements, C_{10} (diamond) $+H_{17}+Cl=C_{10}H_{17}Cl$, is approximately the same. Turpentine, therefore, possesses a constitution essentially different from that of its isomers. Its excess of energy, as well as that of trimethylene, is dissipated in the formation of compounds and other derivatives; that is to say, in the formation of bodies upon which chemists are accustomed to depend in constructing their actual formulæ, called constitutional, whether on a plane or in space. In virtue of this circumstance it seems permissible to regard trimethylene and turpentine as representing novel types characterised by their mobility and their reserves of energy: these are dynamic isomers.

Apparent Death produced by Alternating Currents. Resuscitation by Artificial Respiration.—A. d'Arsonval.—The author contends that the death produced by an electric shock, known in America by the barbarous name electrocution, is only apparent, and that persons who have been struck by lightning should be treated as if drowned.

Molecular Transformations of Certain Chromium Compounds.—A. Recoura.—The chemical transformation of normal chromic hydrate into the hydrate of the green solutions is produced with an observed liberation of heat of 0·2 cal.

Certain Compounds of Ammonia with Different Salts of Silver. — MM. Joannis and Croizier.— This paper is not adapted for useful abstraction.

Detection of Hydrochloric Acid.—A. Villiers and M. Fayolle.—This paper will be inserted in full.

Geraniol of the Oil of Andropogon Schœnanthus. —Ph. Barbier and L. Bouveault.—The experiments which the authors have undertaken on the essential oil of pelargonium enable them to affirm that this essence is absolutely distinct from that of *Andropogon schœnanthus*, which must not retain the name geraniol, and which the authors propose to call lemonol.

Does There Exist a Digestion of the Albumenoids without Digestive Ferments?—A. Béchamp.—Fibrine is not an immediate principle, but a sort of false microzymic membrane more or less comparable to the membranes and tissues formerly used as ferments. There are no transformations of the albumenoids of the order of digestive phenomena without a physiological cause, and it is not vain to prove that the albumenoids can be reduced to stable definite chemical species.

Bulletin de la Société Chimique de Paris. Series 3, Vols. xi.-xii., No. 6.

A New Apparatus for Exhaustion.— L. Étaix.— This paper cannot be reproduced without the accompanying figure.

Correction Concerning a Communication from G. Bouchardat.—Ph. Barbier.—A question of priority.

Certain Points of Stereochemistry. Observations Concerning a Memoir by M. Bouveault.—A. Combes. —The author contests the novelty of a theorem by M. Bouveault published in the *Bulletin*, xi., p. 144.

Mercuric Phenolates and some of their Derivatives.—Ed. Desesquelle.—On applying to naphthol *β* the method of preparation of mercuric phenolate applied by Romei, the author has obtained a chloro-mercuric derivative, to which he ascribes the formula—

$$Hg\begin{matrix}Cl\\ O.C_{10}H_7,\end{matrix}$$

and which he thinks it will be rational to call "mixed mercuric chloride and naphtholate." If it is susceptible of therapeutic applications, he proposes to name it *β*-sublimonaphthol.

Synthetic Borneols.—G. Bouchardat and J. Lafont. —Not suitable for useful abstraction.

Determination of Secondary Products Containing Nitrogen Formed During Combustion in Air. — Lojos Ilosway de Nagy Iloswa.—The author considers it to follow from his data that on burning in air one and the same volume of coal-gas and of hydrogen, one and the same weight of nitrogen is converted into ammonia. On burning one and the same of coal-gas or of hydrogen, the nitrogen transformed into nitrous acid will also have approximately the same weight. But on burning carbon monoxide, we find nearly 2½ times more nitrogen in the state of nitrous acid than in the former case. On burning 1 kilo. of these gases, we find the most nitrogen in the state of ammonia, and in the state of nitrous and nitric acids in the products of the combustion of hydrogen, but we find only the fourth of this quantity if we burn coal-gas, and about one-twentieth if we burn carbon monoxide. On burning in air wood charcoal, whether it has been dried or heated to redness, the quantity of nitrogen contained in the nitrous and nitric acid collected is almost equal to that of the product. In all probability on burning the same weight of coke there is not much more nitrogen oxidised, and the difference is due to experimental error. The ammonia formed during the combus-

tion of charcoal and coke is merely a product of the decomposition of these substances. Otherwise it would be difficult to comprehend why the weight of the ammonia formed should vary according to the degree of heat. On burning coal-gas and hydrogen, the sum of the equivalents of the acids is from 11 to 15 times greater than the figures of the equivalents of the ammonia. The sum of the equivalents of the acids formed by the products of the combustion of coke also exceeds that of the ammonia, whilst on burning charcoal dried at 120° and heated to 600° the sum of the equivalents of the ammonia. In all cases the sum of the equivalents of nitric acid exceed that of the equivalents of nitrous acid; only the experiments made with carbon monoxide prove the contrary. Hydrogen peroxide is one of the constant components of the air, and occasions almost always the reactions ascribed to ozone. It is not possible to establish on a scientific basis the determination of the atmospheric ozone.

Constitution of Oils for Reds.—Paul Juillard.—Sulphuric acid in reacting upon ricinic acid gives rise to ricino-sulphuric acid, dioxystearo-sulphuric acid, bibasic diricinic acid, mono-basic diricinic acid, dioxystearic acid, and isoricinic acid.

Analysis of a Decayed Cheese; Extraction of a Ptomaine.—Charles Lepierre.—Among the group of the bases precipitated in the cold by copper acetate, the author separated a crystalline base, $C_{16}H_{23}N_2O_4$. It is inodorous, bitter, slightly acid to phenolphthalein, soluble in alcohol, and sparingly soluble in water. It forms a hydrochlorate, chloroplatinate, and chloraurate. The specific rotatory power (in water) is $(a)_D = +3°$. Its salts are precipitated by sodium phosphomolybdate in acid solutions, by picric acid, mercuric chloride, but not by tannin. The toxic action occasioned by the consumption of certain cheeses seem to be due at once to the principles developed by the microbia and to the microbia themselves.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 99.

Comparative Study of Analytical Procedures employed in the Determination of the Carbon in Iron.—Prof. Walther Hempel.—The methods employed in analytical practice may be divided into three groups. The first group includes procedures in which the carbon is separated from the iron and then determined by combustion. This group includes the two procedures of Berzelius, that of the same chemist modified by Pearse and Greath (?), the method of Boussingault, that of Eggertz, that of Weyl, of Berthier, and of Saernshaem. In the second group the iron is separated by volatilisation at a high temperature. Here comes the procedure of Berzelius and Woehler, and that of Deville. In the third group the iron is submitted to direct combustion without a preliminary elimination of the carbon. This group includes a process by Berzelius, also the methods of Regnault, of Kudernatsch, of Bruner-Gmelin, and of Wiborg, Reis, Thoerner, Lunge, and Marchlewski, an improved procedure by Wiborg. Hempel's new method cannot be intelligibly described without the accompanying figures. In criticising the methods the author remarks that in grey cast-irons there are often differences in the proportion of carbon extending to 0·2 per cent according as the sample is taken from the surface or the interior of a block.

The original method of Berzelius generates hydrogen carbide in quantities which cannot be neglected.

The same method, as modified by Pearse and Greath, gives results approximately satisfactory.

The second method of Berzelius is scarcely practical.

The procedure of Eggertz involves losses of carbon, and is to be rejected.

Weyl's method gives satisfactory results.

The method of Berthier is too tedious. The procedure of Saernshaem is not preferable.

The method of Berzelius and Woehler gives very good results.

The sodium chloride used in Deville's method always contains traces of hydrocarbons which may falsify the results.

The following method of Berzelius, like those of Regnault and of Kudernatsch, involve the difficulty of requiring the iron to be in the state of fine powder.

In the methods of Gmelin, as well as those of Wiborg, Reis, Thoerner, Lunge, and Marchlewski, losses are always encountered.

The methods of Berzelius (Pearse, Greath, and Ulgren), the galvanic process of Weyl, and the method of Berzelius and Woehler, merit the preference.

Revue Universelle des Mines et de la Metallurgie. Vol. xxvi., No. 1.

This issue contains no chemical matter.

MISCELLANEOUS.

Diffusion of some Gases through Caoutchouc Sheets.—A. Reychler.—The author's explanation of this process is that we have to do here not with true diffusion but with occlusion. The gases concerned, carbonic or sulphurous acids, or mixtures of both, have a strong affinity for caoutchouc, and are taken up on one side by the sheet, whilst they escape into the air on the other side.—*Bull. de la Soc. Chimique.*

A Contribution to Decisions on Drinking-Waters.—Dr. Victor Vedrödi.—The author, on examining waters taken from depths of 40, 120, and even greater depths in Artesian wells bored in compact clays, found ammonia, nitric acid, and occasionally nitrous acid. At Deheczin water from the depth of 832 metres was found to contain, in 100 grms. earth extracted with 1 litre of water, 75 m.grms. organic matter, a trace of chlorine, traces of ammonia, and a strong trace of nitrous acid. It seemed impossible that these impurities could be derived from sewage or from polluted superficial drainage. He argues that waters should not be condemned on the evidence of organic matter, ammonia, nitrous acid, chlorine, &c., without a previous examination of the locality.—*Chemiker Zeitung.*

Quantitative Determination and Separation of the Cacao Alkaloids.—W. E. Kunze.—The determination of the total alkaloids is suitably effected by precipitation with phosphomolybdic acid in a sulphuric solution. The precipitate is decomposed with baryta water, the liquid is treated with carbonic acid, evaporated down, and the alkaloids are extracted from the dry residue with boiling chloroform. The separation of the alkaloids can be conveniently and very accurately effected gravimetrically or volumetrically by means of silver theobromide. The process offers the advantage that after the completion of the determination the identity and the purity of the alkaloids isolated can be determined. The determination is simple and is easily executed, and gives more exact results than the methods previously published.—*Zeitsch. fur Anal. Chemie*, xxxiii., Part 1.

The National Home-Reading Union.—The aim of the National Home-Reading Union may be summed up in a short sentence—to render study attractive. A happy experience of four successive summers has proved to the Council of the Society that there is no other means by which this can be accomplished so effectively as by taking the student to the locality which most abundantly illustrates his work. Geology can best be taught on the top of a mountain or in a Derbyshire cave; the beginnings of history acquire an objective reality as one stands within

the circle at Stonehenge. An English cathedral is a text-book of architecture. Botany is irresistibly interesting when the teacher accompanies his pupils through a wood or over a moor. The Summer Assemblies of the N. H. R. U., which are open to all, whether members of the Union or not, for the small fee of seven shillings, will be held this year at Buxton, in Derbyshire, during the last week in June, and at Salisbury during the first week in July. The programmes are far too long for insertion, but the general scope of the meetings may be gathered from the following abridged lists of lectures and subjects. At Buxton the Inaugural Address will be given by the Ven. Archdeacon Farrar and lectures by the Rev. Dr. John Hunter, of Glasgow, Professor Seaman, the Rev. R. Harley, F.R.S., Canon Hicks, Miss Wakefield, Dr. T. J. Lawrence, Mr. Walter Crane, and others. The geological excursions will be conducted by Mr. J. C. Marr, M.A., F.R.S., Sec. G.S., who will also lecture on "The Building of the Pennine Chain." The Duke and Duchess of Rutland have graciously allowed a garden-party to be held at Haddon Hall. Conferences upon various social and educational subjects have been organised, and will be addressed by the Rt. Hon. W. Woodall, M.P., the Bishop of Southwell, Lady Laura Ridding, and others. The object of the Meeting at Salisbury will be the study of the monuments with which the district abounds, illustrative of the Archæology, Art, and History of Early England. "From Stonehenge to Salisbury Cathedral" Lectures will be given by Mr. York Powell, M.A., Mr. J. R. Tanner, M.A., Mrs. Brownlow, Professor Baldwin Brown, the Dean of Salisbury. Mr. J. Wells, M.A., Sir Robert Ball, LL.D., F.R.S., Professor Jebb, M.P., and General Pitt Rivers. Archæology and Geology will be in the charge of Dr. Humphry Blackmore, F.G.S., Professor T. McKenny Hughes, F.R.S., and Baron Anatole von Hügel, M.A. Mr. A. C. Seward, M.A., will lecture on Botany and accompany the excursions as botanical guide. The Marquis of Bath is President of the Salisbury Assembly, the Rt. Hon. W. Woodall, M.P., of the Meeting at Buxton. Full programmes are to be obtained from the Secretary to the N. H. R. U., Surrey House, Victoria Embankment, London, W.C.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Estimating Sulphate of Lead.—Will you kindly allow me to ask through the medium of your "Notes and Queries" column whether there is a good method of estimating large and small percentages of $PbSO_4$ in mixtures of oxides of lead by means of $BaCl_2$?—C. H.

Estimation of Gold.—In the Second Edition (1886) of "Select Methods in Chemical Analysis," by William Crookes, reference is made to Mr. Skey's method of determination of gold in low grade ores in New Zealand. Has anything further been developed in that line of experiment?—A. H. Willis, A.M., M.E., Denver, Col.

MEETINGS FOR THE WEEK.

Tuesday, 12th.—Medical and Chirurgical, 8.30.
—— Photographic, 8.
Thursday, 14th.—Royal, 4.30.
—— Mathematical, 8.
Friday, 15th.—Quekett Club, 8.

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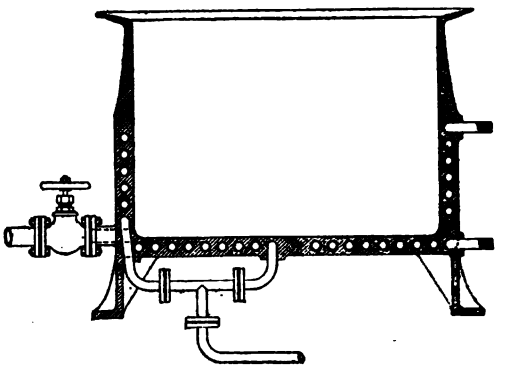

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says:—
P. 316. "An improved vessel for boiling oil, and suitable for many other kindred purposes, has been recently described by T. Frederking (Chemical News, London). A coil of stout piping is arranged in a casting mould, so that the molten metal forming the pan is cast round the coil, much as is done in the case of the water-tuyeres of a blast furnace. Steam at any pressure [or any other heating medium] being passed through the coil, the pan is heated up proportionately without any danger, the pressure bearing solely on the piping and not on the metal pan itself, whilst the well conducting metal walls allow the heat to pass readily. Temperatures up to 350° and 400° C. can be thus obtained."
Messrs. KALLE & Co., Manufacturers of Aniline Colours, Biebrich (Rhine), in their letter of November 22nd, 1893, say:—
"We have tried your Patent Vessel during three months, and have come to the conclusion that it has realised all our expectations. The working pressure of steam has been up to 10 atm. additional pressure; the heating was as efficient and as quickly developed as if the tubes were in the fluid. After having turned off the steam we used the same pipes immediately for cooling by sending water through them, and the vessel, after continued use in this way, proved itself free from cracks or fissures."
Messrs. C. and G. MÜLLER, Rixdorf, near Berlin, S.O., in their letter of December 22nd, 1893, say:—
"Concerning the Patent Vessel which you delivered to us, we beg to inform you that it has been in work four months to our entire satisfaction. The security in working with high pressure is especially satisfactory. With your Patent Vessel we are able to put through much larger quantites of tallow in less time than with our previous plant."
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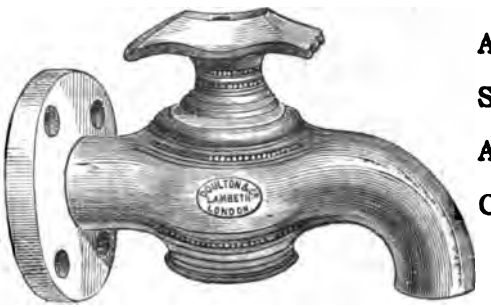

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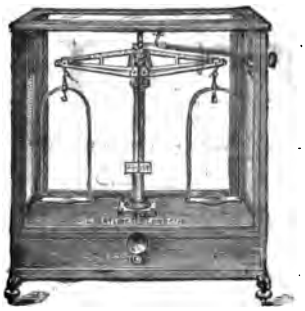

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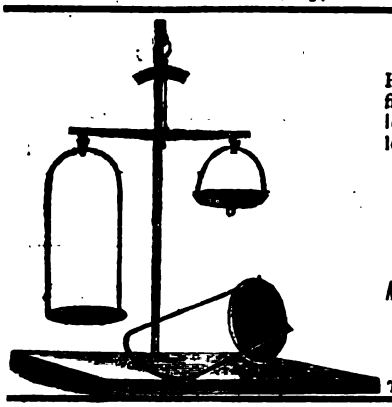

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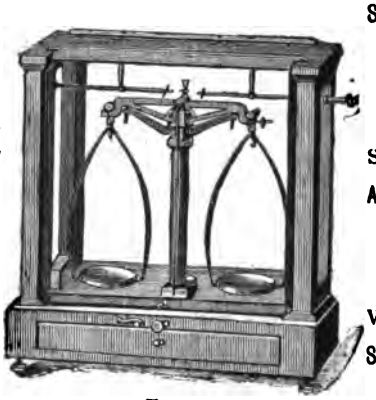

FIG. 3a.

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Vol. LXIX., No. 1803.

SOME MODIFICATIONS OF BECKMANN'S EBULLIOSCOPIC APPARATUS.

By C. E. LINEBARGER.

The second model of the well-known apparatus devised by Beckmann (*Zeitschr. für phys. Chemie*, viii., 223, 1891), for the determination of molecular masses of substances from the boiling-points of their solutions, seems to leave little to be desired as regards convenience in the performance and accuracy in the results of experiments carried out with it. The main objection in its construction is to be found in the difficulty experienced in adding the substance, the molecular mass of which is to be determined, to the solvent in ebullition. With liquids, indeed, the use of the so-called Beckmann's pipette permits of the introduction of substance into the ebullioscopic tube through

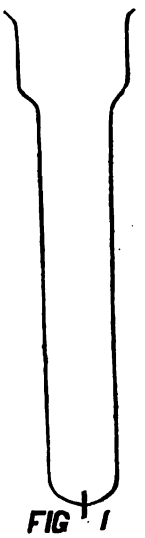


FIG 1

the tube of the reflux condenser, the only danger of error being the liability that the vapours of the solvent may condense upon the end of the pipette and in this way contaminate the liquid contained in it. This error, though slight, is not negligeable in accurate work. Solids can be shot down through the condenser into the solvent, but, in order that a portion may not cling to the sides of the tube, they must be brought into the form of pastilles or fragments free from dust; powders and the like invariably stick to the glass, so that it is very difficult to introduce them quantitatively into the solvent. Two other ways of getting the substance under examination into the boiling solvent are —(1) the lifting of the thermometer cork enough to permit of the introduction of the substance; and (2) the severing of the connection between the ebullioscopic tube and the condenser, so that the substance may be thrown in. Both of these methods occasion the loss of the solvent, and thus introduce so great an error that their use is not to be recommended.

All the difficulties felt in the introduction of the substance into the boiling solvent can be easily obviated by the use of a vertical reflux condenser, so that the substance may be dropped down without coming into contact with the sides of the tube. This necessitates an alteration in the shape of the ebullioscopic tube. The shape found most advantageous is shown in Fig. 1 (furnished by F. O. R. Götze, in Leipsic). Instead of the side tube the mouth of the main tube is melted on to another wider tube. A good cork is fitted to this widened part, through which two holes are bored, one for the thermometer, the other for the tube of the condenser. The one through which the thermometer passes is made somewhat slantwise, so that the bulb of the thermometer may occupy the axis of the tube. The tube of the condenser is best rather short and wide, good results having been found with the following dimensions;—Internal diameter, 12 m.m.; length, 190 m.m. With such a condenser even a light powder can be dropped into the ebullioscopic tube without danger of its adhering to the sides of the condensing tube.

In order to reduce to a minimum the escape of the solvent during an experiment, it is advisable to make use of the following device. The upper end of the condensing tube is fitted with a perforated cork, through which passes a tube of about 8 m.m. external diameter, closed at its lower end and drawn out into a short capillary at its uppe

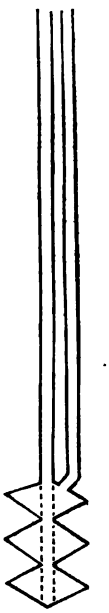


FIG 2

end. About an inch or two from the lower end a tiny hole is blown in the side of the tube. This tube is pushed through the cork so that the small opening is 2 or 3 m.m. below the cork. The tube thus prepared is filled with the solvent to the level of the side aperture and fitted into the condensing tube. In this way all vapours which may escape the cooling action of the condenser before escaping into the outside air must pass through this little opening into an atmosphere already saturated with the vapour of the solvent. Prompt condensation takes place, and the vapours which otherwise might have escaped are returned to the solution. If solvents be employed, such as alcohol, &c., which attract moisture from the air, it is well to put the upper end of the tube just described in communication with a chloride of calcium tube. Indeed, such a tube may be made from a straight chloride of calcium tube with rather long stem by melting together the lower end and blowing a hole in the side.

Another modification consists in the substitution of an inner cooler for the usual Liebig's cooler. This is made in the shape shown in Fig. 2, out of thin sheet copper, which may be gold-plated in order to resist better the

action of certain solvents. With such a condenser the condensing tube may be taken quite short without a disturbing loss of the solvent occurring. I have determined the loss incurred by its use for several usual solvents.

Ether.—22·228 grms. of ether were boiled for four hours. The loss in weight was found to be 0·078 grm.; accordingly in one hour only about 0·8 per cent.

Alcohol.—After 23·640 grms. of absolute alcohol had been kept vigorously boiling for four hours a diminution in weight amounting to 0·633 grm. had taken place; that is, about 0·6 per cent per hour.

Water.—31·613 grms. of water, after boiling for five hours, had lost 0·376 grm., corresponding to a percentage loss of less than 0·3 per cent an hour.

It is apparent from these experiments that the inner cooler is serviceable even with low boiling solvents, although naturally it is better adapted for such as have but slight tensions of vapour.

The modifications here described are indeed slight, but they facilitate greatly the use of the apparatus. Especially is this the case with the new form of ebullioscopic tube, by the use of which the vexatious sticking of substance to the sides of the condensing tube is entirely prevented.

Ecole des Mines, Paris,
June 7, 1894.

THE ACTION OF CYANIDE OF POTASSIUM ON GOLD AND SOME OTHER METALS AND MINERALS.*

By G. A. GOYDER, Adelaide, S.A.

(Concluded from p. 270).

Iron.

Some small pieces of iron wire were placed with 1 per cent KCyAq in an inverted test-tube; after remaining in three days no trace of gas had been given off.

The solution was then replaced with six per cent KCyAq, with the same result, nor was there any evolution of gas when the apparatus was heated over the water-bath.

Another sample of fine soft iron wire was polished with sand-paper, and made into a helix; weighed 0·3592 grm., and placed with 6 per cent KCyAq in an inverted test-tube; after remaining in thirteen days no gas had been evolved, and the wire remained bright and unchanged; it was taken out, washed with water and alcohol, warmed, dried, and weighed exactly the same as when put in. The solution, on testing for ferrocyanide of potassium, after acidification, gave no reaction.

The same wire was then attached to a piece of platinum wire, and both together placed in the 6 per cent KCyAq; after remaining in six days, no gas had been given off, and the wire, on weighing, was found to have the same weight as before.

The same piece of iron was now introduced into a combustion tube, through which a current of dry hydrogen was passed, the tube was ignited and then allowed to cool, the current of hydrogen still being kept up; the iron was then transferred without contact with air into a tube of 6 per cent KCyAq, which was inverted as usual. No gas was given off during eighteen days' immersion, and no iron was dissolved, the solution affording no reaction for ferrocyanide.

August 26, 1892.—Some 6 per cent KCyAq was put in a basin, a gold leaf was added, and the solution stirred continuously; all the gold dissolved in twenty minutes; a piece of fine soft iron wire was then added to the solution, another gold leaf added, and the solution stirred constantly, till all dissolved after twenty minutes. The iron did not appear to be at all coated with gold, nor to have retarded the solution in the least.

September 6, 1892.—The iron wire was removed from the solution, washed with water and alcohol, warmed, and weighed, the weight being exactly the same as when first put in, and the appearance unchanged.

A piece of aluminium wire placed in the solution became coated with a distinct layer of gold in less than half an hour.

Part of the solution on testing was proved to contain the auri cyanide of potassium, $KAuCy_4$.

Further experiments were made with steel wire and ordinary hoop iron with the same result.

It would therefore appear that ordinary black iron may be used for making the vessels used in the MacArthur-Forrest process, without fear of incurring loss of gold or cyanide therefrom.*

It was now deemed advisable to try whether a more active form of iron would have any effect on the KCyAq; therefore some metallic iron, in a fine state of division, was prepared by passing dry hydrogen over ferric oxide, heated in a combustion tube to redness; the hydrogen was passed until the tube was cold, and the iron produced was shaken, without undue exposure to air, into a test-tube of 6 per cent KCyAq, a loose asbestos plug fitted into the tube, and the tube inverted as usual. Minute bubbles of hydrogen were given off very slowly, but continuously, for seventeen days, when the tube had become filled with gas. A drop of the solution tested with ferric sulphate and HCl gave a strong reaction for ferrocyanide. The gas was tested and found to be all absorbed by palladium black, proving it to be hydrogen.

This experiment was repeated, using ferric oxide, prepared by precipitating ferric chloride with ammonia and washing thoroughly, in order to be certain that no alkaline metal could be present in the reduced metal; the result was the same as in the last experiment.

A similar result was obtained on reducing the ferric oxide by heating in a current of carbonic oxide, the evolution of gas, however, being rather less rapid, but as the gas given off was proved to be hydrogen, and not carbonic oxide, the presence of gas could not be due to occlusion.

Nickel.

September 9, 1892.—A piece of sheet nickel was placed with 6 per cent KCyAq in an inverted test-tube, weight 0·5885 grm.

September 23, 1892.—The solution appeared of an orange colour, with a slight precipitate like ferric hydrate; no gas given off.

October 27, 1892.—Same as last date. Nickel taken out, washed, dried, and weighed 0·5853 grm., dissolved 0·0032, returned to solution without tube and loosely covered.

November 26, 1892.—Nickel taken out, washed, dried, and weighed 0·5730 grm.; dissolved since last date, 0·0123 grm.

Some nickel oxide was reduced in a combustion-tube, at a red heat, by hydrogen, and transferred without contact with air to a test-tube of 6 per cent KCyAq, and the tube inverted; hydrogen commenced to come off at once, 12 p.m., and continued to come off briskly till 5 p.m. on the same day, when the tube was full. The solution was of a dark orange-yellow colour, and on cencentration and cooling yielded crystals of K_2NiCy_4.

September 29, 1892.—A deposit of nickel was made in a glass tube by reduction from nickel carbonyl, $Ni(CO)_4$, according to Mond's process, and the tube, air not being allowed to enter, was filled with 6 per cent KCyAq; the nickel deposited covered the greater part of the inside of the tube.

October 14, 1892.—A few bubbles of gas given off.

November 7, 1892.—A little more gas collected; the

* From the *Transactions of the Australasian Institute of Mining Engineers*, vol. i. Meeting held in April, 1893.

* The iron might, however, be attacked by other salts present in conjunction with the air.

nickel appeared to have dissolved more near the bottom than the top.

January 10, 1893.—Volume of gas collected still increasing, but small. Most of the nickel dissolved.

This experiment cannot be regarded as quite conclusive, as the gas given off may have been occluded in the nickel, and was not analysed. The action, however, appeared to be the same as with the nickel reduced by hydrogen, but very much slower.

Cobalt.

September 15, 1892.—Some oxide of cobalt was reduced by hydrogen and transferred when cold, without contact of air, to a test-tube filled with 6 per cent KCyAq, and the tube inverted; hydrogen began to come off at once, but not nearly so quickly as with the nickel reduced in the same way.

November 3, 1892.—Tube nearly full of hydrogen. Part of the solution was tested and proved to contain cobalticyanide of potassium.

Nickel and cobalt thus appear to be intermediate between iron and zinc, or copper, in their action with KCyAq, nickel having the most energetic action of the three metals, Ni, Co, and Fe.

Aluminium.

A piece of aluminium wire weighing 0·1545 grm. was placed with 6 per cent KCyAq in an inverted test-tube, and gave off hydrogen more freely than any other metal tried; after being in for five hours the tube was full of gas. The aluminium was taken out, washed, &c., and weighed 0·1441 grm., 0·0104 grm. having been dissolved. The hydrogen evolved measured 19·5 c.c. at 13° C. and 758·2 mil., equal to 0·00164 grm. hydrogen—

$$\text{as Al } 28 : \text{H } 1 :: 0{\cdot}0104 \text{ to } 0{\cdot}00037 \text{ and } \frac{0{\cdot}00164}{0{\cdot}00037} = 4{\cdot}43,$$

so that probably four atoms of hydrogen are evolved by the solution of one of Al in KCyAq. Several formulæ suggest themselves to explain the reaction taking place in this case, but further experiment will be necessary to prove which is the correct one. The solution contained a bulky precipitate of aluminium hydrate, and some ammonia, and it would appear, according to a paper by R. Varet on "The Action of Metals on Salts dissolved in Organic Liquids" (*Comptes Rendus*, cxiv., 224), that the double cyanide of aluminium and potash is very unstable, and decomposed by contact with water, and could not be obtained sufficiently pure for analysis in consequence.

Argentite (Sulphide of Silver).

Butters and Clennel remark (*loc. cit.*):—"Ores containing sulphide of silver and sulphide of copper produce considerable decomposition of cyanide, the copper being partly dissolved as sub-sulpho-cyanide, the silver, however, remaining unattacked. In two experiments carried out by Mr. William Bettel, Chief Chemist of the Robinson Gold Mining Co., and one from the Albert Silver Mine, containing 30 ozs. of silver and 10 per cent of copper, it was found that no extraction of silver occurred, the metal being present as sulphide."

MacArthur states (*loc. cit.*) that "sulphuretted hydrogen and sodium sulphide precipitate silver from cyanide solution," and further that "silver as sulphide was not very easily dissolved in some cases; usually it could be extracted. A 30-ton lot might be quoted, where the silver (as sulphide) and the gold were equally well extracted." These two statements by MacArthur are directly contradictory (*vide* Note, p. 262)

A sample of argentite was obtained for me by Mr. G. C. Klug of this department from the Australian Broken Hill Consols Silver Mine. It was crushed fine and digested several times with ammonia to remove copper carbonate, &c., washed, and then digested with shaking for about a minute with 6 per cent KCyAq and filtered at once, as the undissolved mineral had changed from almost black to orange. To part of the solution HNO_3 was added, and this produced a black precipitate which by further testing proved to consist of silver and sulphur. The portion of the ore left undissolved consisted of sulphides of antimony and lead.

This experiment proves that at least some of the mineral silver sulphides are easily dissolved by KCyAq, and it is probable that in the experiment made as above by Mr. Wm. Bettel, the whole of the cyanide present was exhausted in dissolving the copper, but that a second or third extraction would have dissolved the silver sulphide. This point has been alluded to, as it is not impossible that the cyanide process may in the future be applied to some of the silver ores of Australia, especially if it should be produced at a lower cost.

NOTE.—It is obvious that much still requires to be done before the action of metals and minerals on KCyAq can be fully explained, and I have indicated some points which will occupy me at my first leisure. I had intended to experiment with the metals produced by electrolysis, but have not yet been able to do so. One experiment was, however, made.

The electro-deposition of gold and silver from a weak solution of the double cyanides in 1 per cent KCyAq takes place quantitatively with a moderate current, about 0·006 ampère per square inch of surface. During the deposition, part of the KCy is decomposed, and carbonates of potassium and ammonia formed, but the gold and silver are all deposited before all the KCy is decomposed, as it was found by an experiment made that the gold from a 1 per cent KCyAq solution could be deposited twice by the current and re-dissolved each time by interrupting the current without the addition of more KCy. Experiments will be made to ascertain how many times these alternate actions can take place before the solution becomes too weak to re-dissolve the gold. Mercury and cadmium are deposited by the same strength of current as silver and gold, but copper requires a stronger current, and is not deposited till all the KCy has been decomposed.

It would appear also that iron might be used for both the negative and positive terminals, although the slight action on the positive one might make it advisable to use some other material.

The great advantages of electro-deposition in this case would be—the gold and silver would be obtained at once in an almost pure state.

The solution would be less weakened during the precipitation of these metals than probably by any other process, and the strength at once restored by addition of KCy.

No foreign matter is introduced as is the case when zinc is used.

ON THE ORIGIN OF GOLD NUGGETS.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

(Continued from p. 268).

PURE sponge gold was sealed up for three months with ammonium sulphide with no reaction; but both potassium and sodium sulphides gave black precipitates, and a strong reaction for gold was given by the liquid in each case; the ammonium sulphide heated for six and a half hours at 145° to 180° C. was unchanged, but reacted strongly for gold; the solution of potassium sulphide also reacted and the glass was much attacked; further, there was a black precipitate of gold; the sodium sulphide acted much more feebly. Other salts and solvents were used but with no very striking results.

Egleston states, p. 72, that "the same conditions which

* A Paper read before the Royal Society of New South Wales, September 6, 1893.

cause the solution of the gold in certain cases, cause also the solution of the silica." And "many of the causes which produce the precipitation of the gold would also cause the reduction of soluble sulphates to insoluble sulphides, the gold being retained within the mass. This would account for the almost constant presence of gold in pyrites."

"No single agent is so powerful a solvent of gold as chlorine. Very few drainage waters are free from some compound of it, and no soil is without the nitrogenous materials necessary to set the chlorine free, and therefore capable of attacking the gold and rendering it soluble. . . . The readiness of filtration through the relatively easily permeated gravel causes the gold to precipitate so rapidly that there is no time for any but a mammillary deposit, which in vein deposits the extreme slowness of the deposition allows the gold to assume the crystalline shape."

Melville Attwood, E.M., in a paper "On the Source or Origin of Gold found in Lodes, Veins, or Deposits" (Report of the State Mineralogist of California, 1884, vol. viii., p. 773) quotes that "M. Laur ("On the Origin and Distribution of Gold in California," communicated to the Academy of Sciences, Paris) mentions having found metallic gold in deposits, *evidently* derived from some hot springs."

A. Daubrée, in his "Les eaux souterraines a l'epoque actualle" (Paris, 1887, p. 33), says:—"Plusieurs géologiques (J. P. Laur, A. Phillips, et Egleston) ou cru reconnaître qu'en Californie de l'or se dépose encore actuellement, particulierement dans des graviers. On prétend aussi avoir trouvé ce metal dans l'eau de Louèche et plus récemment, d'apres Göttl, dans l'eau de Gieshübl et dans celle de Carlsbad."

Posepny, "Zur Genesis de Metallseifen (*Œsterr. Zeits. f. Berg. und Huttenwesen*, 1887, xxxv.), is of opinion that the formation of large masses of gold in the vein are more easily accounted for than in alluvial deposits.

E. Cohen ("On the Genesis of Alluvial Gold," *Jahr. f. Min.*, 1889, i., Ref. 439—440, from *Mit. Ver. f. Neuvorpommern u. Rügen*, xix., 198) is of opinion that the greater part of alluvial gold is derived by the disintegration of older deposits, but that separation from solution also occurs in a subordinate manner.

Mr. H. P. Washburn, in a paper entitled "A Theory on the Formation of Gold into Specks and Nuggets" (*Trans. N. Z. Inst.*, 1889, p. 400), opposes the hypothesis that nuggets have been formed *in situ* in alluvial deposits.

Composition of Vein and Alluvial Gold.

In the preceding references there are several statements as to the greater purity of alluvial gold over vein gold, and this is by many assumed to be a proof that the nuggets and other forms of alluvial gold have had a different origin to the vein gold and that the alluvial gold has been deposited in the way suggested by Selwyn and other writers.

If we examine some of the assays of vein and alluvial gold, we shall see that there are differences, but that they are not very material, and, further, the vein gold is sometimes richer than the drift gold.

Selwyn and Ulrich ("P. G. G. and Min. of Vict.," 1866, p. 42) refer to the greater richness of alluvial gold.

D. C. Davis ("Metalliferous Minerals and Mining," London, 1880, p. 50), in speaking of the gold-bearing drift of the Sierra Nevada, says:—"The particles of gold are found of larger size and contain more silver at the bottom than at the top of the ancient drift, and are worth less by two shillings and sixpence per ounce. It is supposed that their difference in quality is caused by the larger size of the fragments below resisting more effectually the action of sulphuric acid which, set free by the decomposition of pyrites, has eaten the silver out of the smaller grains at the top of the deposit."

He also says, p. 36:—"Gold is most plentiful in it (drift in the Urals) where the drift is most largely charged with iron;" and Brough Smyth, in a "Report on the Gold Mines of the S.E. Portion of the Wynaad, &c." (London, 1880) states that "the gold obtained in the Wynaad is unequal in fineness, that from the soils being of the best quality. It has been observed in other countries that the finer the particles of the gold procured from alluvial deposits the higher is the quality."

P. Nisser ("On the Geol. Distribution of Gold, with special reference to some Auriferous Rocks in South America," *Trans. Phil. Institute Vict.*, iv., 1860, read March 30, 1859) points out (p. 17) that in the province of Antioquia, North Granada, the gold from the veinstones differs very greatly from the alluvial gold; the former averaging 14⅓ carats fine, and the latter 18 to 22 carats. He states that W. Birkmyre found that vein gold from Clunes, Victoria, was poorer than the alluvial gold, and that the same thing was observed by other assayers; and he finally concludes that since the South American alluvial gold differs so much from the vein gold that it must have had a different origin.

Bernhard von Cotta in his treatise "On Ore Deposits" (New York, 1870), in speaking of the placer deposits of the Urals, says that the gold is generally more or less argentiferous, the amount of silver varying, according to G. Rose's examinations, between 0·16 and 38·74 per cent. It has been sometimes thought that the placer gold was purer (less argentiferous) than that extracted from deposits *in situ*, but G. Rose has shown that such is not the case in the Ural mountains. He found that the amount of silver was very variable in both cases, although the highest amount of silver was found in gold from veins, which contained, even in the same lode, very variable quantities."

Mr. Geo. Foord, F.C.S., of Melbourne, could find no difference between the quality of the internal and external portions of nuggets; but in one case he found a vein which was of a greenish yellow in the centre, from the larger amount of silver present in that part of the gold.—Brough Smyth, "Gold Fields and Mineral Statistics of Victoria," p. 359.

Mr. Birkmyre, p. 371 of the same work, yoints out that the "Welcome" nugget, weighing 184 pounds 9 ounces, gave him 23 car. 3½ grs. of gold, or 99·20 per cent, or it was nearly as rich as the finest gold dust, viz., 23 carats 3¾ grs.

The following analyses of gold from the North Transvaal (E. Cohen, *Jahr. f. Min.*, 1889) show a slight difference between the vein and the alluvial gold; but much importance cannot be attached to it:—

	Residue.	Ag.	Au.	Cu.	Fe.	Total.
1. Vein gold ..	0·02	5·16	94·48	0·25	trace	99·91
2. Alluvial gold	0·78	6·49	91·38	0·09	,,	98·74
3. ,, ,,	0·07	5·64	95·16	—	,,	99·87
4. ,, ,,	0·07	4·57	94·87	0·11	,,	99·62

1. Vein gold, Button's reef, Marabastad, North Transvaal.
2. Alluvial gold, Button's Creek, derived from above.
3 and 4. Alluvial gold, in flakes and grains.

Experiments.

Freshly fractured pieces of the following sulphides were placed in cylinders of the photographer's gold toning solution (15 grains of the double chloride of gold and sodium in 15 ounces of water), viz., iron pyrites, molybdenite, mispickel, galena, copper pyrites, blende, argentite, &c.

In some cases the sulphide reduced the gold at once and became gilt or coated with the reduced gold, either as a bright coherent deposit or else as a dull ochre-coloured one. Successive quantities of the gold solution were added from day to day as it became colourless, and in this way quite thick and strong deposits of gold were formed on the sulphides.

In the case of the molybdenite, MoS_2, the gold deposit

was at first lustrous and metallic, but as time went on it became of a dead brown aspect, although this under the microscope was seen to be made up of brilliant metallic points of light. Blue and white oxides of molybdenum separated out.

The deposit on the mispickel was not compact and coherent like that on the molybdenite, galena, and other minerals, but loose and easily rubbed off.

The deposit on the iron pyrites was also bright and metallic looking at first, but as it thickened it became dull and ochre-like in colour.

The deposit on the galena was similar to the above; under the microscope, the surface, as in other cases, is seen to be minutely mammillated, and it is on that account that, to the unassisted eye, the gold has a dull brown or ochre colour.

(To be continued).

METHODS OF ANALYSIS OF BUTTER.*

Microscopic Examination.

Place a small portion of the fresh samples, taken from the inside of the mass, on a slide, add a drop of pure sweet oil, cover with gentle pressure, and examine with a one-half to one-eighth inch objective for crystals of lard, &c. Examine the same specimen with polarised light and a selenite plate without the use of oil. Pure fresh butter will neither show crystals nor a parti-coloured field with selenite. Other fats melted and cooled and mixed with butter will usually present crystals and variegated colours with the selenite plate.

For further microscopic study dissolve 4 or 5 c.c. of the fat in 15 c.c. of ether in a test-tube. Close the tube with a loose plug of cotton-wool, and allow to stand twelve to twenty-four hours at room temperature (20° to 25°). When crystals form at the bottom of the tube they are removed with a pipette, glass rod, or tube, placed on the slide, covered, and examined. The crystals formed by later deposits may be examined in a similar way.

Sampling.

If large quantities of butter are to be sampled, a butter trier or sampler may be used. The portions thus drawn, about 500 grms., are to be perfectly melted in a closed vessel at as low a heat as possible, and when melted the whole is to be shaken violently for some minutes till the mass is homogeneous.† A portion is then poured into the vessel from which it is to be weighed for analysis, and should nearly or quite fill it. This sample should be kept in a cold place till analysed.

Determination of Water.

One and five-tenths to 2·5 grms. are dried to constant weight at the temperature of boiling water in a dish with flat bottom, having a surface of at least 20 c.m.²

The use of clean dry sand with the butter is admissible, and is necessary if a dish with round bottom is employed.

Determination of Fat.

The dry butter from the water determination is dissolved in the dish with absolute ether, or with 76° benzine. The contents of the dish are then transferred to a weighed Gooch crucible with the aid of a wash bottle filled with the solvent, and are washed till free from fat. The crucible and contents are heated at the temperature of boiling water till the weight is constant. The weight of fat is calculated from the data obtained.

Alternate Method for Fat.

Water may be determined by drying the butter on asbestos or sand, and the fat extracted by anhydrous alcohol-free ether. The extract, after evaporation of the ether, is heated to constant weight at the temperature of boiling water and weighed.

Determination of Casein and Ash.

The crucible containing the residue from the fat determination, consisting of casein and ash, is covered and heated, gently at first, gradually raising the temperature to just below redness. The cover may then be removed, and the heat continued till the contents of the crucible are white. The loss in weight of the crucible and contents represents casein, and the residue in the crucible mineral matter. In this mineral matter, dissolved in water slightly acidulated with nitric acid, chlorine may be determined gravimetrically with silver nitrate, or volumetrically, using potassium chromate as an indicator.

Determination of Salt.

The amount of the butter or butter substitute to be taken is from 5 to 10 grms.; weigh in a counterpoised beaker-glass. The butter is placed, in portions of about 1 grm. at a time, in the beaker, these portions being taken from different parts of the sample. Hot water is now added (about 20 c.c.) to the beaker containing the butter, and after it has melted the liquid is poured into the bulb of a separating funnel. The stopper is now inserted and the contents shaken for a few moments. After standing until the fat has all collected on top of the water, the stop-cock is opened and the water is allowed to run into an Erlenmeyer flask, being careful to let none of the fat globules pass. Hot water is again added to the beaker, and the foregoing process is repeated from ten to fifteen times, using each time 10 to 20 c.c. of water. The resulting washings contain all but a mere trace of the NaCl originally present in the butter. The sodium chloride is now determined in the filtrate by a standard solution of $AgNO_3$, using a few drops of a saturated solution of potassium chromate as an indicator.

Specific Gravity.

Standardisation of Flasks.—Use a small specific gravity flask of from 25 to 30 c.c. capacity. The flask is to be thoroughly washed with hot water, alcohol, and ether, and then dried. After cooling in a desiccator, the weight of the flask and stopper is accurately determined.

The flask is filled with freshly boiled and still hot distilled water, and placed in a bath of pure distilled water. The water of the bath is kept in brisk ebullition for thirty minutes, any evaporation from the flask being replaced by the addition of boiling distilled water. The stopper* is then inserted, the flask removed, wiped dry, and, after it is nearly cooled to room temperature, placed in the balance, and weighed when balance temperature is reached.

Weight of Fat at the Temperature of Boiling Water.—The flask is emptied of its water, rinsed with alcohol and ether, and dried again for a few minutes at the temperature of boiling water. It is then filled with the dry, hot, fresh-filtered fat, which should be entirely free from air bubbles, and replaced in the water-bath, kept for thirty minutes at the temperature of boiling water, removed, and treated as above. The weight of fat having been determined, the specific gravity is obtained by dividing it by the weight of water previously found.

Example.

	Grms.
Weight of flask No. 22, dry	10·0197
Weight of flask No. 22, plus water	37·3412
Weight of water	27·3215
Weight of flask No. 22, plus fat	34·6111
Weight of fat	24·5914

Specific gravity = 24·5914 + 27·3215 = 0·90008.

* Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (American) at its Meeting at Chicago, August, 1893.

† The mass must be sufficiently solidified to prevent the separation of the water and fat after it is placed in the bottle.

* The stopper should be kept for a few minutes before use in hot distilled water.

The weight of the flask dry and empty, and the weight of water at boiling temperature contained therein, may be used constantly if great care be taken in handling and cleaning the apparatus.

Example.

	Grms.
Weight of flask No. 10, dry and empty ..	10·0028
Weight of flask after three weeks' use ..	10·0030

Alternate Method of Standardising Flasks.—Formula for calculating the volume V, in cubic centimetres, of a glass vessel from the weight, P, of water of temperature, t, contained therein, and the volume, V', at any other temperature, t' (from Landolt and Börnstein's "Physical-Chemical Tables," p. 39, Table 17).:—

$$V = P\frac{\rho}{d}$$

$$V' = P\frac{\rho}{d}\left[1+\gamma(t'-t)\right]$$

ρ = Weight (in brass weights) of 1 c.c. of H_2O *in vacuo*. (This is so nearly 1 that it will not affect the result in the fifth place of decimals, and may therefore be disregarded). Hence the formula stands—

$$V' = P\frac{1}{d}\left[1+\gamma(t'-t)\right]$$

d = Density of water at temperature t.

γ = 0·000025, the cubical expansion coefficient of glass.

Melting-point.

The apparatus for determining the melting-point consists of (1) an accurate thermometer for reading easily tenths of a degree; (2) a cathetometer for reading the thermometer (this may be done with an eye-glass if held steadily and properly adjusted); (3) a thermometer; (4) a tall beaker glass 35 c.m. high and 10 c.m. in diameter; (5) a test-tube 30 c.m. long and 3·5 c.m. in diameter; (6) a stand for supporting the apparatus; (7) some method of stirring the water in the beaker; for example, a blowing bulb of rubber, and a bent glass tube extending to near the bottom of the beaker; (8) a mixture of alcohol and water of the same specific gravity as the fat to be examined.

Manipulation.—The discs of the fat are prepared as follows:—The melted and filtered fat is allowed to fall from a dropping tube from a height of 15 to 20 c.m. on a smooth piece of ice floating in water. The discs thus formed are from 1 to 1·5 c.m in diameter and weigh about 200 m.grms. By pressing the ice under the water the discs are made to float on the surface, whence they are easily removed with a steel spatula, which should be cooled in the ice water before using.

The mixture of alcohol and water is prepared by boiling distilled water and 95 per cent alcohol for ten minutes to remove the gases which they may hold in solution. While still hot the water is poured into the test-tube already described until it is nearly half full. The test-tube is then nearly filled with the hot alcohol. It should be poured in gently down the side of the inclined tube to avoid too much mixing. If the tube is not filled until the water has cooled, the mixture will contain so many air bubbles as to be unfit for use. These bubbles will gather on the disc of fat as the temperature rises and finally force it to the top.

The test-tube containing the alcohol and water is placed in a tall beaker containing water and ice until cold. The disc of fat is then dropped into the tube from the spatula, and at once sinks until it reaches a part of the tube where the density of the alcohol-water is exactly equivalent to its own. Here it remains at rest and free from the action of any force save that inherent in its own molecules.

The delicate thermometer is placed in the test tube, and lowered until the bulb is just above the disc. In order to secure an even temperature in all parts of the alcohol mixture in the vicinity of the disc, the thermometer is moved from time to time in a circularly pendulous manner.

The disc having been placed in position, the water in the beaker-glass is slowly heated, and kept constantly stirred by means of the blowing apparatus already described.

When the temperature of the alcohol-water mixture rises to about 6° below the melting-point, the disc of fat begins to shrivel, and gradually rolls up into an irregular mass.

The thermometer is now lowered until the fat particle is even with the centre of the bulb. The bulb of the thermometer should be small, so as to indicate only the temperature of the mixture near the fat. A gentle rotatory movement should be given to the thermometer bulb. The rise of temperature should be so regulated that the last two degrees of increment require about ten minutes. The mass of fat gradually approaches the form of a sphere, and when it is sensibly so, the reading of the thermometer is to be made. As soon as the temperature is taken, the test-tube is removed from the bath and placed again in the cooler. A second tube, containing alcohol and water, is at once placed in the bath. The test-tube (ice water having been used as the cooler) is of low enough temperature to cool the bath sufficiently. After the first determination, which should be only a trial, the temperature of the bath should be so regulated as to reach a maximum of about 1·5° above the melting-point of the fat under examination.

The distilled water for floating the piece of ice on which the discs are made should be recently boiled, to free it of all air particles.

The edge of the discs should not be allowed to touch the sides of the tube. This accident rarely happens, but in case it should take place, and the disc adhere to the sides of the tube, a new trial should be made.

Triplicate determinations should be made, and the second and third results should show a near agreement.

Example.

Melting-point of sample of butter:—

First trial	33·15° C.
Second trial	33·05° C.
Third trial	33·00° C.

(To be continued).

SEPARATIONS OF METALS.*

Separation of Lead and Cadmium.

By E. HINTZ.

After the boat has been repeatedly heated in the manner described (p. 235), and the sublimates have been driven into the receivers, the tubes are permitted to cool in a slow current of bromine vapour. The boat is then drawn out of the tube, and, with the yellowish melt of lead and cadmium bromide which it contains, it is placed in a porcelain capsule, covered with chlorine-water, and evaporated to dryness on the water-bath with occasional renewals of the chlorine-water. The contents of the boat are thus converted into the more readily soluble chlorides.

The lead and cadmium chlorides are then dissolved in hot water, the boat rinsed out by means of the washing-bottle, and the clear solution is poured into a beaker. Here the lead is precipitated at a boiling heat with boiling dilute sulphuric acid. An equal volume of alcohol is added, and the lead sulphate, after prolonged subsidence and after the liquid has become perfectly clear, is filtered

* *Zeitschrift für Analytische Chemie.*

off, ignited, and weighed. The filtrate is sufficiently concentrated to expel the alcohol. The cadmium is precipitated with sodium carbonate and determined as cadmium oxide.

The liquid from the receivers, containing the tin and the bismuth, is evaporated down in a large capsule, the residue is rinsed with nitric acid into a large porcelain crucible,, again evaporated down on the water-bath as far as possible, and finally the free sulphuric acid is expelled in an air-bath. For the entire removal of the sulphuric acid, the crucible is finally directly ignited with a full flame. This complete elimination of the sulphuric acid by ignition is unconditionally necessary, since otherwise the stannic acid is not entirely converted into the insoluble state. The residue, after prolonged ignition, is then subjected to prolonged and repeated heating with nitric acid on the water-bath, in order to bring all the bismuth oxide into solution. The stannic acid, perfectly insoluble in dilute nitric acid (1 : 3), is filtered, preferably through a double filter, so that it may not pass through turbid, and finally washed with water containing nitric acid until all the bismuth is extracted. The bismuth in the nitric solution is then precipitated at the heat of ebullition by ammonium carbonate, whereby any large excess of free nitric acid must first be removed by evaporation.

The ignited bismuth oxide may, under certain circumstances, contain small traces of silica, as it attacks the porcelain crucibles. In such a case, the ignited oxide is again dissolved in nitric acid, the silica is filtered off, and the bismuth is again precipitated with ammonium carbonate.

In the analysis of Wood's metal on the more simple method by the direct conversion of the metals into sulphides in a porcelain boat, the authors proceed as follows:—

A capacious porcelain boat, containing 4·5 c.c. (7 c.m. in length, and 1·5 c.m. in breadth), is half filled with pure pulverised sulphur. Upon this substratum the small cuttings of metal are uniformly distributed, and another stratum of sulphur is superimposed. The boat, thus charged, is introduced into a wide combustion-tube (20 to 22 m.m. in internal diameter). A current of dried carbonic acid is allowed to pass through the tube until all the air is expelled, and heat is then applied with a moving flame, commencing at the beginning of the boat. The sulphur quickly melts down with the metal, forming a metallic sulphide. The excess of sulphur is heated to ebullition, and driven further towards the end of the tube. When the entire contents of the boat have thus been converted into sulphide, the boat may, for the sake of certainty, be once or twice again filled with sulphur and the same operation repeated. This is, however, rarely requisite. It is then merely necessary to let the boat cool in the current of carbonic acid, to draw it out, and to transfer it to the bromising apparatus which is standing ready. The combustion in the current of bromine is then carried out as above described.

It is thus possible to effect a most accurate analysis of Wood's metal within the limit of one and a half to two days.

P. Jannasch and W. Remmler have extended the above method to the separation of lead from tin and from antimony.

In heating lead sulphide and tin sulphide in a current of bromine vapour, tin-bromide, which is easily volatile, passes over into the receivers, whilst the lead-bromide remains entirely in the boat, and is converted into lead sulphate, and determined as above described.

The hydrochloric solution of tin which has collected in the receivers is reduced to a small volume with the addition of nitric acid, the residue is transferred to a weighed porcelain capsule of a medium size, and evaporated as far as possible. After the stannic acid thus obtained has been repeatedly evaporated with fuming nitric acid, it is finally heated in an open air-bath for the expulsion of the sulphuric acid, again moistened with from 1 to 2 c.c. of strong nitric acid, evaporated, ignited, and weighed. The procedure may be greatly simplified if the metals are at once converted into sulphides by fusion along with sulphur.

The weighed substances are placed in the apparatus, covered with from 6 to 10 parts of pure pulverised sulphur, and, lastly, intermixed by shaking. A current of sulphuretted hydrogen perfectly dried by means of glycerin and granulated calcium chloride is conducted through the apparatus, and the sulphur is gradually melted and heated to ebullition. The sulphur reacts upon the metals, and after its expulsion there remains a mixture of sulphides. It may be advisable to repeat the entire operation. The apparatus is now connected with a bromine vapour generator and the requisite receivers, and the tin and the antimony is slowly distilled off at the gentle heat of a small gas flame.

By this method, however, the complete sulphurising of metallic tin and of ignited tin oxide is effected only with great difficulty. Metallic tin, in the form of foil or of raspings, must be fused for some hours with sulphur if it is to be entirely converted into sulphide. The authors therefore attempted to make the sulphur more effective by an addition, and accomplished this object by means of iodine. If we add to the sulphur from 10 to 15 per cent of iodine, comminuted tin may be perfectly combined with sulphur in the shortest time.

Stannic acid can be also easily combined with sulphur on this method, even after previous prolonged ignition.

The combination of antimony with sulphur is still more easily effected.

(To be continued.)

ON SODIUM PEROXIDE.

By TH. POLECK.

I had induced my two assistants, HH. Hoehnal and Kassner, to study the action of sodium peroxide and its analytical applications for a number of cases, and I now communicate the results hitherto obtained. Proceeding from the researches formerly carried out by Prof. Kassner and Kwasnik on the action of hydrogen and barium peroxides, a quite analogous behaviour was observed with sodium peroxide, though the processes took place more energetically.

Salts of mercury, silver, and gold are reduced with liberation of oxygen, but platinum chloride not until $PtCl_6H_2$ has been previously decomposed by a salt of silver, when both chlorides are reduced to metals. The behaviour of the double platinum salts of the alkalis and alkaline earths is similar, platinum being reduced only after the addition of a salt of silver.

Sodium peroxide precipitates ferric hydroxide from the ferrous and ferric salts, but manganese peroxide is at once thrown down from the salts of manganese and cobaltic oxide from those of cobalt; permanganic acid is reduced to manganese peroxide, chromic oxide is oxidised to chromic acid, salts of uranium yield sodium peruranate, $U_2O_8Na_4+8H_2O$. This salt is precipitated by alcohol and decomposed by hydrochloric acid, with a liberation of chlorine. If the yellow solution of this uranium salt is boiled for a considerable time it turns to a vinous red, and a salt insoluble in water, $U_2O_7Na_2$, separates out. Bismuth hydroxide and its salts are quickly oxidised to bismuthic acid.

With potassium ferricyanide sodium peroxide behaves like the corresponding hydrogen and barium compound, reducing the ferricyanide to ferrocyanide. This behaviour is therefore parallel to Prof. Kassner's method for the volumetric determination of this substance. Thus in the sodium peroxide employed in this investigation there were found 83·62 per cent of the pure compound.

The separation and quantitative determination of iron

on the one hand and of manganese and chrome on the other is easily and completely effected in the wet way and gives good results. Iron is precipitated as ferric hydroxide, manganese as peroxide, whilst chrome passes into solution as chromic acid, which is then reduced by means of alcohol and the chrome weighed as chromic oxide.

The analysis and separation of tin, antimony, and arsenic is very easily effected in the sulphur compounds precipitated by sulphuretted hydrogen and then dissolved in ammonium sulphide. The latter solution is either evaporated down in order to remove the excess of ammonium sulphide, or the metallic sulphides are once more precipitated. They are then covered with water in a tall beaker and sodium peroxide is added in small quantities until the colour of the sulphides has entirely disappeared, which takes place in the course of a few minutes. The oxidation of the metals and of the sulphur is complete. The oxygen compounds of the metals are separated by known methods.

This method of oxidising the metallic sulphides has the advantage over that by nitric acid, as in toxicological cases it admits at once of the use of the Marsh apparatus.

The opening up of pyrites and blende for analytical purposes has been already attempted by different methods, and the procedures have been described. By the use of equal parts of sodium peroxide or sodium carbonate the oxidation is completely and smoothly effected, forming an excellent analytical method, if the choice of the vessels did not present difficulties. Leaving porcelain quite out of the question, silver, platinum, and nickel crucibles are severely attacked. A platinum crucible lost in every operation from 0·05 to 0·1 grm. weight.

The action of sodium peroxide upon lead oxide does not yield sodium orthoplumbate, but metaplumbate—

$$PbO_3Na_2+4H_2O.$$

The formation of orthoplumbate, $Pb(ONa)_4$, corresponding to the orthoplumbates of the alkaline earths discovered by Kassner, has not yet proved practicable.

Iodine, on heating with sodium peroxide, is very easily and rapidly converted into acid sodium periodate—

$$I_6O_6H_3Na_2,$$

sparingly soluble in water. Its identity was ascertained by its behaviour with sulphuric acid, hydrogen sulphide, its behaviour with salts of lead, barium, and silver, and by its sparing solubility. By treating the normal silver periodate with bromine, concentrating the solution in the first place at about 60° and then *in vacuo*, we obtain free periodic acid, HIO_4+2H_2O, in finely developed crystals, to the extent of 65 per cent of the theoretical yield of sodium periodate.

The oxidation of carbon compounds in alcoholic solution seems to promise good results, as alcohol is not attacked by sodium peroxide, whilst ether is at once ignited.

The examination of the further applications of sodium peroxide in analysis will be continued.—*Ber. der Deutsch. Chem. Gesell.*, xxvii., No. 8.

ON THE

DETERMINATION OF PHOSPHORIC ACID.*

By H. PEMBERTON, Jun.

Last autumn I described a process for determining phosphoric acid by titration of the ammonium phosphomolybdate with standard alkali (*Journal of the Franklin Institute*, cxxxvi., p. 362). The ratio between the P_2O_5 of the precipitate and the standard alkali was determined and found to be 23·2 molecules of Na_2O to one molecule of P_2O_5. Upon this ratio, as determined by direct analysis, the standard solution was prepared of such strength that 1 c.c. should be equal to 1 m.grm. of P_2O_5 by diluting 326·5 c.c. of normal alkali to 1 litre. The analyses upon which this ratio (23·2 molecules) was determined were carefully made. I was therefore at a loss to know the cause of the variation of this figure from the theoretical ratio of exactly twenty-three molecules of Na_2O. The difference is of more importance than might at first thought be supposed, since the strength of the alkali solution is based upon the figure determined empirically, and not upon the theoretical one. If the 23·2 proportion is wrong and 23 correct, a standard solution based upon the former ratio would give too low results in the proportion of 23·2 : 23·0. Thus a phosphate rock containing 80 per cent bone phosphate of lime would appear by such an analysis to contain only 79·31 per cent.

It was decided, therefore, to repeat this part of the work, and in this re-examination the conditions were the same as those previously existing, except in one particular—the amount of phosphoric acid operated upon was smaller than that previously used. By referring to the original paper it will be found that about 80 c.c. of alkali were used in each of the titrations in question. This represented a quantity of the yellow precipitate much larger than would ever be obtained in the examination of even the richest phosphate rocks; and in operating upon so large a precipitate the liability of error from incomplete washing is great. Any free acid remaining in the precipitate would, of course, result in too high a reading of the burette, with a corresponding error in the standardising of the solution.

The following are the results obtained in this re-examination :—

Some disodic hydric phosphate, bought as chemically pure, was dissolved in hot distilled water, filtered, and crystallised; the crystals were washed, dissolved again in water, and re-crystallised. Of the resulting crop of crystals, about 45 grms. were dissolved in one-half litre of water. The strength of this solution was then determined.

	Weight of Na_2HPO_4 solution.			
I.	20·0814 grms.	gave	0·7581 grm.	$Na_4P_2O_7$.
II.	17·9585 ,,	,,	0·6778 ,,	$Na_4P_2O_7$.
III.	36·9115 ,,	,,	1·1652 ,,	$Mg_2P_2O_7$.

The magnesium ammonium phosphate precipitate was filtered, dissolved in acid, and re-precipitated by ammonia.

By a coincidence each of these three determinations gave precisely the same result, viz. :—

Table I.

	Grms. P_2O_5 in 10 grms. of solution.
I.	=0·2014
II.	=0·2014
III.	=0·2014

Therefore 10 grms. of the phosphate of soda solution contained 0·2014 grm. P_2O_5.

Weighed portions of this same solution were now precipitated by ammonic molybdate, thoroughly washed, and titrated. The results are given in Table II.

Table II.

I.	II. Grms. Na_2HPO_4 solution taken.	III. Equivalent to grms. P_2O_5.	IV. C.c. of KHO solution used.
A	2·0410	0·04110	41·05
B	2·3710	0·04775	47·70
C	2·2920	0·04616	46·20
D	2·4690	0·04972	49·60

Dividing the figures in Column III. by those in Column IV., and multiplying the result by 100, we obtain the number of m.grms. corresponding to 100 c.c. of the KHO solution as follows :—

* Read at the Chemical Section of the Franklin Institute, Feb. 20, 1894.

Table III.

	M.grms. P_2O_5.
A	= 100·12
B	= 100·11
C	= 99·91
D	= 100·24
Average ..	= 100·09

Therefore 100 c.c. of the KHO solution neutralises an amount of the yellow precipitate corresponding to 100·09 m.grms. of P_2O_5.

The standard acid was now titrated against the standard alkali, using phenolphthalein as the indicator, whereby the two solutions were found to be of exactly equal strength.

The standard acid was then titrated against pure sodium carbonate, using phenolphthalein at boiling heat.

	Grms. Na_2CO_3 used.	C.c. of acid used.	100 c.c. acid equal to m.grms. Na_2CO.
I.	0·9099	52·95	1719
II.	0·9168	53·35	1719

Therefore 100 c.c. acid are equivalent to 1719 m.grms. Na_2CO_3, and since the alkali solution is of the same strength as the acid, 100 c.c. of it also are equivalent to 1719 m.grms. Na_2CO_3.

As we have already seen by Table III. that 100 c.c. of the alkali are required to neutralise 100·09 m.grms. of P_2O_5 (in the form of ammonium phosphomolybdate), it follows that 1719 m.grms. Na_2CO_3 are required for 100·09 m.grms. P_2O_5.

Dividing each by its molecular weight we have for P_2O_5

$$\frac{100{\cdot}09}{142{\cdot}06} = 0{\cdot}7045,$$

for Na_2CO_3—

$$\frac{1719}{106{\cdot}1} = 16{\cdot}20.$$

Therefore—

$$P_2O_5 : Na_2CO_3 = 0{\cdot}7045 : 16{\cdot}20 = 1 : 22{\cdot}99.$$

In other words, 23 molecules of Na_2CO_3 (or of Na_2O) are required to neutralise the yellow precipitate containing 1 molecule of P_2O_5, and the former figure (that given in my paper of last autumn), 23·2 molecules, is incorrect.

Referring to Table II. of the present paper, it may be stated that in analysis A the yellow precipitate was washed on an ordinary filter without using suction, the precipitate being washed on the filter, transferred to the beaker, and then again filtered and washed. In analysis B of the same table the precipitate was washed on the ordinary filter with the aid of the suction pump. In analysis C and D the precipitates were washed with suction on a porcelain funnel with a fixed perforated plate in it. This form of funnel is known as the Hirsch funnel. (To be had from Bullock and Crenshaw, Philadelphia. A disc of filter-paper of the diameter of an American silver quarter dollar (fifteen-sixteenths inch) is used when employing the smallest size funnel. I can highly recommend this funnel in all cases in which the precipitate is to be titrated. The precipitate presents a perfectly flat surface, is easily and quickly washed, and is readily transferred with the aid of the wash-bottle to the beaker. The funnel can be employed only when using the suction pumps, but it has the advantage of not requiring a platinum cone, and the size of the filter is reduced to a minimum).

As in all cases the results were nearly identical, it is evident that the different methods of washing the precipitate had no influence upon the result. Exactly 23 molecules of Na_2O are required for 1 molecule of P_2O_5. The standard acid is prepared by diluting 323·7 c.c. of normal sulphuric acid to 1 litre. The alkali solution, after removing CO_2 by $Ba(HO)_2$, is brought to the same strength as the acid, volume for volume.

One c.c. of either solution is, then, equal to 1 m.grm. of P_2O_5.

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, June 4, 1894.

Sir James Crichton Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members of the Royal Institution:—Sir George Barclay Bruce, M. Inst. C.E., Sir Thomas D. Gibson-Carmichael, Bart, M.A., Frederick Dye, H.H. Prince Victor Duleep Singh, Major-General Edward R. Festing, R.E., F.R.S., Lennox H. Lindley, B.A., the Duchess of Marlborough. Captain Frederic Lewis Nathan, R.A., Cuthbert Edgar Peek, M.A., F.S.A., Hugh Walsham, M.A., M.B., M.R.C.P.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

Engineering Chemistry: A Practical Treatise for the Use of Analytical Chemists, Engineers, Ironmasters, and Others. By H. Joshua Phillips, F.I.C., F.C.S. Second Edition. London: Crosby Lockwood and Son, 1894.

The book now before us is not intended to cover a very wide field, but is rather restricted to the methods of analysing and valuing some of the most important materials in use by engineers. It has been enlarged by the addition of about eighty pages of matter which would appear best to carry out the author's original plan.

Reddrop's "equivalent system" of reagents is as far as possible used throughout the book. This system having been already fully described in the Chemical News does not need more than a passing notice here.

In Part I. we find full details and instructions for the analysis of the commoner metals and their alloys, as well as the detection and estimation of the impurities generally found therein. Part III. is devoted to the examination of fuels, both solid, liquid, and gaseous, and some interesting comparisons are given of the relative costs, &c., of various systems which have been or now are in use for replacing coal with either of the latter fuels. Part IV., on water and water analysis, rather lightly passes over this subject. More attention and fuller details might with advantage have been given; for instance, the indigo method of estimating nitrates and nitrites—a very rapid and exact process—is not given at all. Oils and grease are the next materials dealt with, not only from the lubricating point of view, but also as illuminants; after which in Part VII. we come to gas and gasworks products.

A subject which has recently attracted a good deal of attention is that of explosives, but little more than the manufacture of nitro-glycerin and dynamite is here discussed. A list of the composition of a few of the many patent explosives now in existence is given, but considering to what abominable uses these may be put by a certain class of individuals who possess that dangerous article "a little knowledge," we think it is as well that the methods of manufacture have been omitted.

In the appendix which completes the work we note a useful table for ascertaining quickly the amount of any constituent sought, from the form in which it is weighed, the factors by which the atomic weights must be multiplied being given for a large number of compounds.

Methylated Spirit: A Compendium for the Retailer and Laboratory Director, with some Information for the Public. By Algernon Warren. Bristol: J. W. Arrowsmith. London: Simpkin, Marshall, and Co.

Since 1891 chemists have had good cause to complain of the restrictions with regard to the purchase of pure methylated spirit. There are a certain lot of irritating conditions to be complied with before any one is allowed to buy pure methylated spirit; the purpose for which it is required must be stated, and an accurate record kept of the quantity used—this record, together with the permit to buy, to be produced whenever demanded by the excise officer. It is in order to make it easier for users to obtain the article required that Mr. Warren has compiled this pamphlet.

The form of application is shown, and all the various conditions of purchase and use are set forth and commented upon.

The pamphlet can be obtained from the publishers, price 4d.

Essai de Chemie Synthétique. ("Essay on Synthetical Chemistry.") By F. C. Barlet. Paris: Chamuel and Co., 1894.

The evolution of matter and the periodicity of the elements are matters of absorbing interest, and have attracted the close attention of many of our foremost scientific men. The science of chemistry affords the best field for speculation on these matters, being an exact science, and standing, so to speak, midway between mechanics and biology.

In the latest contribution to our ideas on this subject, M. Barlet, after reviewing the work done by previous thinkers, elaborates certain theories in a peculiar and novel manner. He accepts to a certain point the arguments brought forward by Mr. Crookes and shown diagramatically in the well-known zig-zag and spiral conical figures; but here he stops, and considers the matter from an entirely different standpoint. Instead of projecting the curve as a spiral figure of eight, he proposes a horizontal projection on a plan perpendicular to the axis; this shows a curve just like a watch-spring, but is divided into four quadrants by two diameters. On either side of the vertical diameter we find represented two half-oscillations of Mr. Crookes, the two other halves being shown on the other side, these two halves corresponding to the para- and dia-magnetic states, the horizontal diameter separating alternately a period of cooling and re-warming, so that if we represent the hot and cold states by $+a$ and $-a$, and the para- and dia-magnetic states by $+m$ and $-m$, we get an arrangement in this style—

$$\begin{array}{c|c} (-m)\,(-a) & (+m)\,(+a) \\ \hline (-m)\,(+a) & (+m)\,(-a) \end{array}$$

The author now introduces the four terms so largely used by the ancients to express differences in the state of matter, viz., *fire*, *earth*, *air*, *and water*, and to each of these *elements* he assigns a governing place in his quadrant, thus:—

Fire	Earth
Water	Air

From this basis the author proceeds to develope his theory as to the affinities and otherwise of the different elements for each other, and substitutes in the four sections *strong acids*, *strong bases*, *weak acids*, and *unstable acids*. We do not propose to follow him through all his reasoning; suffice it to say that the outcome of his arguments is to confirm the periodicity of elements propounded by Newlands and Mendeleeff, and afterwards explained by Crookes. The whole subject is one of great fascination, but one about which we may truly say that it is a mystery beyond human intellect to solve; speculations are not satisfactory, and we *know* nothing.

CORRESPONDENCE.

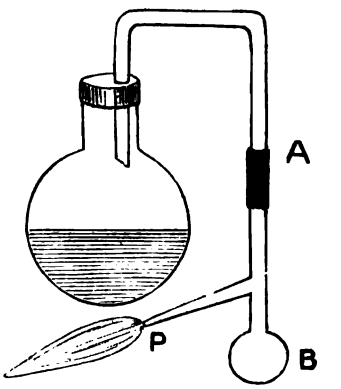
SPIRAL BLOWPIPE.

To the Editor of the Chemical News.

Sir,—The following blowpipe was designed when gas was not available; it may be of interest to others.

An ordinary round bottom flask is fitted with a cork carrying a tube arrangement as shown in the sketch. At A the tube is broken and joined with a piece of very flexible indiarubber tubing. The flask is nearly half filled with methylated spirit, and a candle or spirit-lamp held underneath until it begins to boil. The vapour issuing from P takes fire and is driven out into a jet. The candle or lamp may now be withdrawn, the heat from the jet being sufficient to keep the spirit boiling.

If the indiarubber tubing at A is properly fitted, the lower part, A B, is pushed back when the vapourisation is



too rapid, and the flame being withdrawn a little from the flask, the boiling slows down. Thus it is self regulating. The bulb, B, collects the few drops of spirit that condense, but condensation is much lessened if the tube and upper part of the flask be covered with asbestos.

If the tube be pushed further through the cork, the point, P, is lowered, and now if a spirit-lamp be placed underneath the flask the jet blows into it and a flame is obtained for fusions in estimations (sulphur in iron ores, &c.) where coal-gas is objectionable. The arrangement may be supported by a clip round the neck of the flask, or by the flask fitting into a small tripod.—I am, &c.,

Harry Brearley.

The Laboratory, Norfolk Works,
Sheffield, June 7, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 22, May 28, 1894.

Detection of Hydrochloric Acid.—A. Villiers and M. Fayolle.—In a previous paper the authors mention that in presence of bromine the reaction which they propose is more or less masked by the formation of bromine chloride. This formation may be avoided and as great a sensitiveness may be obtained as in the absence of hydrobromic and hydriodic acids by proceeding as follows:—The hydracids, having been separated by means of silver nitrate, the precipitate is washed and then conveyed into

a small flask, into which, after having decanted the liquid, there are added 10 c.c. of water and 1 c.c. of pure ammonia. The flask is shaken for some minutes if it is required to find considerable quantities of hydrochloric acid. If traces have to be sought for the ammonia is left for some hours in contact with the precipitate. At this dilution the ammonia does not dissolve appreciably the silver bromide, and has no action at all upon the silver iodide. On the contrary, the chloride dissolves to a considerable extent (even totally if very little hydrochloric acid is present), especially if we wait a sufficient time so that the bromide which is dissolved at first may be displaced by the chloride. It is now required to reproduce the hydrochloric acid in the ammoniacal liquid. Zinc and sulphuric acid give bad results, and small quantities of chlorine may disappear entirely whilst the zinc is dissolving, probably from the presence of some impurity in the zinc. It is preferable after having filtered the ammoniacal liquid to heat to ebullition until the odour of ammonia has entirely disappeared, and to add an excess of a solution of sulphuretted hydrogen. We then boil again so as to reduce the volume of the liquid to about 10 c.c., and filter the liquid into a flask. The operation is completed as previously directed. It is well not to make use of corked bottles which may retain traces of chlorides, but to use flasks sealed to the escape tube, fitted with a ground glass stopper traversed by a safety tube so as to avoid resorptions. The complete freedom of the reagents employed from hydrochloric acid must be checked by a blank experiment. By operating thus we may detect the slightest traces of chlorides in the bromides and iodides, in bromine and iodine, &c. In order to obtain a solution of hydrobromic acid not giving any sign of the presence of hydrochloric acid, we have saponified with water a hydrobromic ether carefully rectified. In the case of an analysis the differences of colourations will readily enable us to distinguish if we have to do with notable quantities of hydrochloric acid or with mere traces. The application of this process pre-supposes the absence of hydrocyanic acid, which gives a precipitate of silver cyanide more soluble in ammonia than the chloride, and which in the further treatment may mask, partly or totally, the chlorine liberated by the permanganate, producing hydrochloric acid and cyanogen chloride. To obviate this cause of error the hydrocyanic acid may be expelled by evaporation along with sulphuric acid until vapours of sulphuric acid begin to appear. The retort is allowed to cool, water is added, and the liquid is distilled afresh. The distillates are united and partially evaporated.

Comparative Study of the Nitrobenzoic Acids.—Oechsner de Coninck.

Action of Aqua Regia (equal volumes of nitric and hydrochloric acids).—The orthonitrobenzoic acid dissolves entirely in heat with a bright yellow colour. The two isomers dissolve partially with the same colour. This reaction allows us to distinguish the nitrobenzoic acids from the amidobenzoic acids, which dissolve with a bright red.

Action of Chromic Acid in a Dilute Aqueous Solution.—No action either in cold or heat (care being taken not to heat to ebullition).

Action of Dilute Hydrochloric Acid.—No change of colour after exposure to sun-light for three months.

Action of Dilute Nitric Acid.—Very similar results to the foregoing. The *meta*-solution ultimately took a light yellow colour.

Action of Dilute Alcohol.—After exposure for three months the *para*-solution took a distinctly yellow colour, whilst the meta-solution took a feeble yellowish tint.

Acetone had no action after an exposure of equal duration.

Constitution of Licareol.—Ph. Barbier and L. Bouveault.—Licareol and lemonol yield almost the same oxidation products, but our reasons for ascribing to them two distinct formulæ are that their aldehydic derivatives are different, as it appears from the different melting-points of their compounds with para-amidophenol. Licareol is active, but lemonol (geraniol) is devoid of rotatory power.

Melting-points of some Phenols and of their Benzoic Ethers.—A. Béhal and E. Choay.—The authors give a table showing the points of fusion and ebullition of the monophenols and their benzoates.

The Rectification of Alcohol.—E. Sorel.—The results of the author are here also given in tabular form.

The Latex of the Lac Tree.—G. Bertrand.—This juice resembles a thick cream of a light blond colour; it has a slight odour like that of butyric acid, and it reddens blue litmus. With alcohol it yields *laccase*, a precipitate chemically identical with the gums, and laccol, a very oxidisable liquid. Lac is produced by the successive influence of oxygen and of diastase.

MISCELLANEOUS.

Pharmacological Research and the Salters' Company.—In connection with the recent foundation of a Research Fellowship in Chemical Pharmacology by the Court of the Salters' Company, the Research Committee of the Pharmaceutical Society announces that the selection of the Salters' Company Research Fellow will take place on July 3 next. Written applications for the Fellowship must be received by the Director of the Research Laboratory, 17, Bloomsbury Square, before June 30.

The "Nibestos" Filter.—We have examined this filter, and find, as its name would imply, that it is a mechanical asbestos filter. Asbestos has long been used in chemical laboratories in connection with the Bunsen and other filter pumps, and is generally recognised as being well adapted for certain classes of filtration. The "nibestos" is extremely simple in its construction and easily cleaned. When it has become foul from long use all that need be done is to replace the old disc of asbestos felt by a new one; this can be done in a few minutes.

Absorption-spectrum of Ozone.—Prof. E. Schöne.—The spectrum consists of thirteen bands of greater or less intensity. The author likewise spoke of the minimum of oxygen capable of spectroscopic detection. The speaker gave also a communication on the results of his spectroscopic researches on atmospheric ozone. In the morning the lower strata of the atmosphere contain less ozone than in the evening. The maximum proportion of ozone occurs in the months of February and March, then there follows a decrease, the minimum being reached in June. During thunderstorms and violent rainfall the spectroscope merely shows the presence of ozone.—*Congress Russ. Nat. and Phys., Moscow*, No. 10.

Chemical Laboratory Labels.—Messrs. Gallenkamp and Co., of Cross St., Finsbury, have brought out a new edition of their laboratory labels, compiled by Mr. W. H. Symons, F.C.S., F.I.C., &c. They are printed in bold type, while the size is such that the whole of the label can be seen from the front of the bottle. The sheets are perforated for convenience of separation, and are well gummed at the back. Formulæ are not given on the labels—a good thing in many cases, for the labels frequently last on the bottles longer than the theories according to which the formula of the contents of the bottles are printed on them. At the same time we could have wished that more duplicates of such names as "nitric acid," &c., had been inserted, to the exclusion of those of the "hydrogen nitrate" class. The theory that all acids are salts of hydrogen may be true and likely to last, but the old-fashioned names of the common acids are more convenient for general laboratory use.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Analysis of Spent Oxides from Gas Works.—May I ask through the medium of your "Notes and Queries" column for a method of analysis for the estimation of sulphocyanides and ferrocyanides in spent oxide from gas works?—Frank H. English.

Prevention of Frosting of Window Panes.—I should be very much obliged for assistance in the following matter. I wish if possible to find out a preventative against the frosting of window panes in the winter time. I have read somewhere of a formula used in Russia for this purpose, but I do not remember what it was. I shall be deeply obliged for any information on this matter.—J. Watson.

MEETINGS FOR THE WEEK.

Wednesday, 20th.—Geological, 8.
—— Meteorological, 8.
—— Microscopical, 8.
Thursday, 21st.—Royal, 4.30.
—— Chemical, 8. "The Specific Character of the Fermentation Functions of Yeast Cells," by Adrian J. Brown. "The Interaction of Lead Sulphide with Lead Sulphate and Oxide," by J. B. Hannay. "The Oxidation of Tartaric Acid in the presence of Iron," by H. J. H. Fenton. "The Relation between the Solubility of a Gas and the Viscosity of its Solvent," by Prof. Thorpe, F.R.S., and J. W. Rodger. And other papers.
Friday, 22nd.—Physical, 5. Exhibition of Photographs of Flames, by Capt. Abney. "An Elementary Theory of Planimeters," by Prof. Henrici. "The Hatchet Planimeter," by F. W. Hill. "A New Integrating Apparatus," by A. Sharp. Other papers if time allows.

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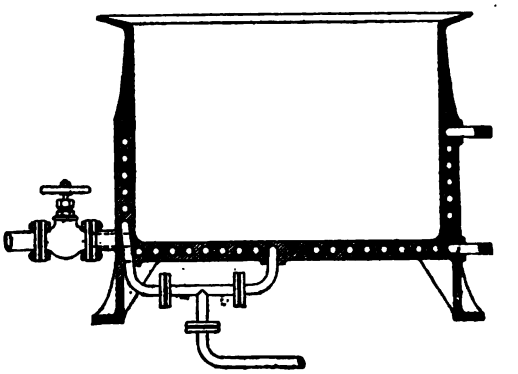

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says:—

P. 316. "An improved vessel for boiling oil, and suitable for many other kindred purposes, has been recently described by T. Frederking (Chemical News, London). A coil of stout piping is arranged in a casting mould, so that the molten metal forming the pan is cast round the coil, much as is done in the case of the water-tuyeres of a blast furnace. Steam at any pressure [or any other heating medium] being passed through the coil, the pan is heated up proportionately without any danger, the pressure bearing solely on the piping and not on the metal pan itself, whilst the well conducting metal walls allow the heat to pass readily. Temperatures up to 350° and 400° C. can be thus obtained."

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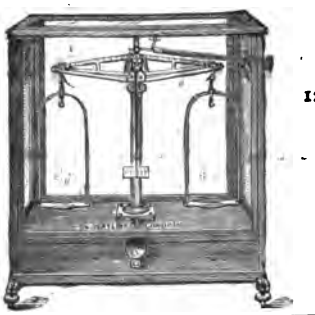

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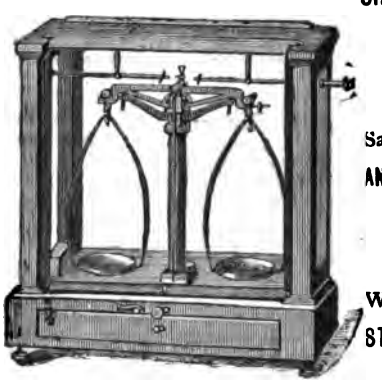

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THE INTERACTION OF QUINONES AND METANITRANILINE AND NITROPARATOLUIDINE.

By Dr. JAMES LEICESTER, F.C.S.,
Lecturer in Chemistry and Metallurgy at the Merchant Venturers' Technical College, Bristol.

THE relationship between quinonedianilide and azophenine has been pointed out by O. Fischer and E. Hepp, (*Ber.*, 1888, 683), who also prepared fluorindine from the latter compound (*Ber.*, 1890, 2789).

In a previous paper (*Ber.*, 1890, 2793; *Chemical Society Abstracts*, 1890, 1445) I gave results of an investigation of the action of orthonitraniline and metanitroparatoluidine on quinone, toluquinone, and naphthaquinone, and showed that in principle the interaction was the same as in the case of aniline and quinone; for example, orthonitraniline and quinone combine to form quinonediorthonitranilide—

$$C_6H_2O_2(NHC_6H_4NO_2)_2\,[CO : NH = 1 : 2 : 4 : 5],$$

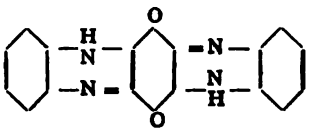
which on reduction with ammonium sulphide yields quinonehomofluorindine.

In addition to the quinonefluorindines certain quinonephenazine derivatives were obtained; these are formed from the nitro-compounds corresponding to quinoneanilide, quinoneorthonitrotoluide yielding quinoneorthomethylphenazine. I have now prepared a number of other quinonephenazines and other quinonefluorindines; in fact, the interaction appears to be a general one in the case of paraquinones. The constitution of these compounds may be inferred partly from the manner in which they are formed and partly from their similarity in properties to the corresponding fluorindines. A number of crystalline compounds have also been obtained by the reduction of anilides and toluides with magnesium; the products are, however, of a somewhat complex nature, and their further investigation is proceeding.

Quinonedimetanitranilide is prepared by heating a solution of quinone and metanitraniline in glacial acetic acid; it crystallises from a mixture of methyl alcohol and benzene, and melts at 295°.

Quinonemetanitranilide is obtained together with the dianilide as a bronze-coloured powder melting at 135°.

Quinonemetahomofluorindine—



is formed by the reduction of the dianilide with ammonium sulphide; it is a brownish black powder, melting above 360°. It affords a brown colour with acetic acid, changing to slaty green and finally to mauve, on the gradual addition of sulphuric acid.

Quinoneparanitrotoluide is obtained in a similar manner as a bluish black, crystalline powder; on reduction with ammonium sulphide it yields a slate-coloured compound which decomposes at 300°.

Quinonediparatoluide is a bronze-coloured substance; on reduction it yields a substance which melts at 320° and dissolves in alcohol, benzene, or acetic acid, forming a dark greenish yellow coloured liquid, exhibiting a green fluorescence.

Thymoquindiorthonitranilide, from thymoquinone and orthonitraniline, crystallises from alcohol and ether in straw-coloured needles, melting at 125°. The phenazine—

$$C_6O_2(C_3H_7)(Me)\begin{matrix}1:4\\6\end{matrix}\begin{matrix}3\\N\\N\end{matrix}\begin{matrix}2:5\\\\\\\end{matrix}C_6H_4$$

derived from it forms grey needles melting at about 320°.

Thymoquindiparanitrotoluide is deposited from absolute alcohol in yellowish red plates melting at 112°; it also crystallises in needles.

Thymoquinorthomethylphenazine—

$$C_6O_2(C_3H_7)(Me)\begin{matrix}N\\N\end{matrix}C_6H_3Me$$

is a greyish white crystalline powder which sublimes at 325°, and dissolves in acetic acid and ether, forming a yellow-coloured liquid.

THE PHYSICAL PROPERTIES OF THE GRAPHITES OBTAINED FROM VARIOUS METALS AFTER THE SEPARATION OF THE SAME BY MEANS OF DILUTE ACIDS.

By H. N. WARREN, Research Analyst.

THE metals of the third group, and especially iron, undoubtedly furnish graphite most readily when maintained at an elevated temperature in contact with carbon; the scales thus separated from the cast metal are possessed of larger magnitude than those obtainable from either nickel or cobalt, both these metals producing graphite of a much finer quality, and in many instances, unless viewed by the aid of a microscope, being undistinguishable from lamp-black, while in all other respects they closely resemble each other. But on further following the group to manganese, a considerable variance is observed; for on dissolving a portion of ferromanganese containing a high percentage of the latter, a graphite is obtained consisting of much thinner scales than by similarly treating cast-iron, and possessed of a distinct brownish tint, being at the same time less readily oxidised. Further, if commercial oxide of manganese is reduced by means of carbon at a high temperature, and the metallic manganese thus obtained be dissolved by the aid of dilute acids, a graphite is produced presenting a perfectly brown colour, the dimensions of the scales being very considerable. I have also frequently observed, after carefully selecting the same, that several of the scales appear decidedly translucent and still less combustible than that obtained from ferromanganese.

Chromeisen thus treated usually gives much brighter scales, and at the same time much harder, than those obtainable in the case of iron, whereas those obtained from cast chromium in appearance approach more closely to silicon, being entirely destitute of any brownish tinge and possessing a semi-metallic lustre, and less energetic to combine with oxygen unless when heated in a current of the pure gas.

The above-mentioned graphites thus produced may be undoubtedly influenced by the difference in fusion of the various metals employed in their production; thus, for instance, chromium being the most difficult of fusion tends to produce a graphite possessing a more stable form than that produced by either iron, nickel, or cobalt. Strange to say, however, each modification may be inverted in the same manner as silicon; thus if a small quantity of pure iron be maintained in the liquid form, and a quantity of the brown modification obtained from manganese be introduced into the liquid metal, and the graphite afterwards separated in the usual manner, it will be found on examination to correspond in every respect with the graphite usually obtained from iron.

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ON THE SPECTRA OF OXYGEN AT HIGH TEMPERATURES.

By J. JANSSEN.

On a former occasion the author has described to the Academy a method founded on the use of electricity, and capable of raising the gases under pressure to a very high temperature without appreciably heating the apparatus in which they are contained.

Before giving an account of the experiments carried out upon oxygen by means of this method, I will first speak of those which have preceded, and in which the temperature, not exceeding 300°, has been reached by means of a series of gas burners acting directly upon the tube containing the oxygen.

The arrangement is as follows:—A tube of steel, 10 metres long, lined within with copper and closed at its ends with glass in the ordinary manner, is placed in a sheet-iron trough which may receive a sand-bath. This trough is heated directly by a set of 100 gas jets. The temperature is measured by means of tubes connected intimately and metallically with the tube.

After having introduced the oxygen at the required pressure, and before heating the tube, we obtain a good spectrum of the luminous source, the sheaf of which traverses the tube, and in this manner we can appreciate the modifications which the rise of temperature may effect in the constitution of the absorption spectrum given by the gas.

We then light the burners and observe the spectrum whilst the temperature and the pressure rise.

When the observations have been made, the burners are extinguished, and the temperature and the pressure are allowed to return to their original condition.

To obtain this result no loss of gas must have occurred in the course of the experiment.

One of the chief causes of these losses is due to the extension—in consequence of the effects of heat—of the pins which unite the pieces of steel forming the joints. To destroy the effects of this expansion, we place between the heads of the pins and the discs which they connect muffs of brass, the length of which has been calculated so that their expansion may compensate that of the pins. We thus obtain for a large extent in the scale of temperatures the same degree of tightness.

The experiments have been made with various pressures of oxygen. They have shown that from common temperatures up to about 300° the bands and rays of the absorption-spectrum of oxygen gas do not undergo any appreciable modification.

But a quite novel fact has appeared. We speak of the very remarkable increase of the transparence of the gaseous columns with the rise of temperature; a transparence shown by a considerable augmentation of the brightness and the extent of the spectrum, especially at the red extremity, which occasions a much more distinct perception of the spectral rays.

We have to return to the theoretic consequences of this important fact.

To rise higher in the scale of temperatures, we then used the tube with a platinum spiral rendered incandescent by the passage of the current.

I shall not revert to the general arrangements of the experiment already described. The incandescence of the spiral is the more difficult to obtain, as the pressure of the gas is higher.

To appreciate the temperature to which the spiral is raised, we may use various methods:—(1) The thermo-electric couple; (2) the observation of the increased pressure of gas occasioned by the passage of the current; (3) the brightness and the extent of the spectrum given by the incandescent spiral when it alone furnishes the light for the spectral apparatus.

The experiment is therefore arranged thus—

The tube being placed vertically, we regulate the lamp which furnishes the sheaf of rays to be analysed, and, lastly, the spectroscope. We then give pressure, and the constitution of the spectrum having been carefully noted, we pass a current of power suitable to the temperature which we wish to obtain. The pressure rises at once, and stops when the equilibrium is established. The spectral phenomena are then compared with those at the commencement.

In the experiments made with the tube of 2—10 metres and with gaseous pressures extending up to 100 atmospheres, we have not observed any appreciable modifications in the constitution of the spectrum. The temperatures reached were estimated as between 800° and 900°.

To reach higher temperatures we are about to increase the power of our electric generators.—*Comptes Rendus*, cxviii., No. 19.

SEPARATIONS OF METALS.*

Separation of Lead and Cadmium.

By E. HINTZ.

(Concluded from p. 284).

The ammoniacal filtrate of lead precipitated by hydrogen peroxide is first concentrated in a capacious capsule of Berlin porcelain until the excess of ammonia is expelled, then heated for some time after adding an excess of nitric acid, and passed through a moistened filter. In the nitric liquid we observe almost regularly the presence of small quantities of insoluble silver compounds, which are reunited with the filtrate by means of treating the filter successively with ammonia, boiling water, and hot dilute nitric acid. The silver is lastly precipitated and determined in the usual manner.

If the lead is precipitated only with a mixture of hydrogen peroxide and ammonia, ½ per cent of lead remains on the average in solution. A certain addition of ammonium sulphate seems to act as advantageously as ammonium carbonate, whence in a sulphuric solution we may obtain correct results by simple precipitation with hydrogen peroxide. The use of a too weak preparation—such as only ½ per cent—is disadvantageous, as is also a too plentiful addition of hydrogen peroxide, whilst the ammonia required does not need to be so carefully measured.

As regards silver the results of the determination agreed with the calculation under almost all circumstances, and the filtrates of silver chloride were always found free from lead. The weighed lead compounds were in turn found also free from any contamination with silver.

When the same method is used for separating silver from bismuth the precipitation of the latter is effected like that of lead in its separation from silver.

As the initial material the author used again the nitrates of both metals dissolved in 50 c.c. water to which have been added 2 c.c. of concentrated nitric acid. The precipitation is then effected in the cold with a mixture of 20 c.c. hydrogen peroxide (2 per cent) and 15 c.c. of strong ammonia. A subsequent addition of ammonium carbonate was here found unnecessary, as no bismuth remained in solution. The further treatment of the pale yellow precipitate of bismuth hydroperoxide, its washing, &c., is effected exactly as above directed for the separation of lead and silver. As for the final weighing of the bismuth the author uses the above-described process of incineration in a platinum crucible.

Separation of Lead and Silver by Chromic Acid in an Ammoniacal Solution.

This separation is effected in the following manner, according to Jannasch (*Berichte*, xxvi., 1500). From 0·5 to 0·6 grm. of each of the nitrates is dissolved in 100 c.c.

* *Zeitschrift für Analytische Chemie.*

of water, the boiling solution is precipitated in a capacious capsule of Berlin porcelain with a 10 per cent solution (also boiling) of potassium bichromate, calculated approximately. Whilst the liquid is being stirred 15 c.c. of dilute ammonia (1 : 3) are added, and the precipitate of lead chromate is heated on the water-bath for from 15 to 20 minutes. When the liquid is cold it is filtered at once, the precipitate is first washed in the cold (three or four times) with weak ammoniacal water, and finally with pure water. The precipitate is easily washed (from four to six times is generally sufficient), and the liquid never passes through the filter turbid. The lead chromate is then weighed in the usual manner.

In order to precipitate the silver the ammoniacal filtrate from the lead chromate is cautiously acidified with nitric acid, avoiding any unnecessary excess, and the silver is thrown down as chloride from the rather dilute solution.

The results were very accurate and the lead chromate contained not a trace of silver.

ON THE

DETECTION OF HYDROCHLORIC ACID.

By A. VILLIERS and M. FAYOLLE.

The detection of hydrochloric acid presents a considerable difficulty if it occurs in the presence of a notable quantity of the other hydracids (the hydrobromic and the hydriodic). The classical method, founded on the production of chlorochromic acid, is applicable only if it is requisite to recognise large quantities of hydrochloric acid. Its use is, further, somewhat dangerous, since violent explosions may be produced in presence of iodides.

Denigès has indicated in 1891 (*Journal de Pharmacie et de Chimie*) a procedure founded upon the partial transformation of chlorine and bromine into alkaline hypochlorite and hypobromite, and on the difference of the colouration produced by the latter in a solution of aniline or preferably of aniline phenate. The iodine and bromine are first eliminated by a treatment with potassium chromate and sulphuric acid, and the chlorine is then liberated by potassium permanganate. These various reactions necessitate the complete removal of the iodine and the bromine. But we have found that in the conditions of this experiment bromine is not without action upon hydrochloric acid. Besides, according to the arrangement indicated by Denigès, we collect only a part of the chlorine evolved by the permanganate. From this twofold reason the results obtained are not constant, and especially the sensitiveness is not very great, though certainly much more so than that of the chlorochromic method.

The method which we propose is more convenient in application, giving constant results, and having a sensitiveness almost indefinite. It permits us to detect with the greatest distinctness the presence of 1 m.grm. of hydrochloric acid, and even of 0·1 m.grm. in presence of more than 1000 parts of a mixture of bromide and iodide. It is founded upon the difference of the action of the halogens upon an acid solution of aniline, iodine producing no apparent reaction, or at least giving a colourless and soluble substitution product, bromine yielding an insoluble substitution product, perfectly white, whilst chlorine forms coloured oxidation products, black and insoluble, if it is in considerable quantity, violet-red in heat, blue in cold, and turning to red after some time in the contrary case.

The sensitiveness of the reagent depends on the acidity of the solution; a solution not acid giving no results, whilst a large quantity of a mineral acid takes no colouration or is quickly decolourised by the heating. It is preferable to use acetic acid, which does not decolourise on heating. We finally adopted the following formula:—

Saturated aqueous solution of colourless aniline	400 c.c.
Glacial acetic acid..	100 „

This liquid may be preserved indefinitely in yellow bottles without becoming coloured.

The liquid under examination is brought by evaporation or by the addition of water to the volume of 10 c.c. and placed in a flask. We add 5 c.c. of a mixture of equal volumes of sulphuric acid and water, then 10 c.c. of a saturated solution of potassium permanganate, and heat gently, turning the gases into 3 to 5 c.c. of the reagent contained in a test-tube immersed in cold water. In the absence of bromine and iodine we obtain thus with 0·1 m.grm. of hydrochloric acid a blue colouration, which is transformed (slowly in the cold, but rapidly in heat) into a more distinct rose colour. If the dose of hydrochloric acid increases, we obtain either a black colouration (very intense with 1 m.grm.) or a black precipitate. The phenomena are different in presence of the other hydracids. In the proportions indicated, the iodine is completely oxidised, and does not pass over on distillation, the bromine carried over forms with the reagent a precipitate, and the chlorine liberated colours the reagent as well as the bromine precipitate, but there is formed at the same time bromine chloride, which does not act like chlorine, and which considerably diminishes both the certainty and especially the sensitiveness of the reaction. Still, we have obtained the following results:—

HI alone	No reaction.
HBr alone	White precipitate, colourless liquid.
0·0150 HI + 0·050 HBr + 0·050 HCl	Deep blue liquid, then violet liquid, black precipitate.
„ „ + 0·010 HCl	Liquid and precipitate blue, and then deep rose.
„ „ + 0·003 HCl	Bluish tint, then distinctly rose.
„ „ + 0·001 HCl	Appreciable tint (rose after some time).

The last colouration is very faint, and nothing is observed on further dilutions. Thus we see these results are sufficient to detect the presence of hydrochloric acid in presence of the other hydracids, even in slight proportions. Thus we may recognise the presence of chlorides in a great number of commercial bromides and iodides. In like manner, on adding at once bromine-water to the reagent the colour of the precipitate obtained can show the presence of chlorine in the bromine, if the former is in a sufficient proportion, as it is often the case in commercial bromine.

Still, the sensitiveness of the procedure is much diminished by the presence of the other halogens. In a future paper we shall show means of remedying this defect, and of obtaining the same sensitiveness as in the case of hydrochloric acid alone.—*Comptes Rendus*, cxviii., p. 1152.

Composition of Cod-liver Oil.—M. Gautier and L. Mourgues.—The volatile bases extracted from cod-liver oil by distillation are:—Butylamine, amounting to one-sixth of the total bases; amylamine, one-third of the whole; hexylamine, a small quantity; dihydrotoluidine, equal to approximately one-tenth of the total bases. The non-volatile bases are:—Aselline; morrhuine forming nearly one-third of the total bases. The acids in combination with the bases are:—Morrhuic acid, a mixture of formic and butyric acids; a small quantity of phosphoric acid derived from the phosphates, phosphoglycerates, and the lecythines.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1894.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, June 8th, 1894.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined two were recorded as "clear, but dull," the remainder being clear, bright, and well filtered.

Again we have to record a deficient rainfall in the valley of the Thames. During the month of May there fell 1·45 inches of rain, whereas the mean fall during 25 years for the same month is 1·95 inches, thus showing a deficiency of exactly half an inch.

Since the winter there has been a steady improvement in the chemical quality of the water supplied by the companies deriving their supply from the Thames. Last month we showed in a tabular form the improvement noticeable in April. The following is a repetition of that table with the addition of the figures for the month of May:—

Averages of the Five Supplies Derived from the River Thames.

1894.	Common salt per gallon.	Nitric acid per gallon.	Hardness, degrees.	Oxygen required per gallon.	Organic carbon per gallon.	Organic carbon per gallon.	Colour. Brown. Blue.
	Means.	Means.	Means.	Means.	Means.	Maxima.	Means.
Mar.	2·285	1·101	15·32	0·052	0·121	0·162	21·3 : 20
April	2·100	0·995	15·00	0·034	0·076	0·108	14·2 : 20
May	2·035	0·839	14·14	0·033	0·073	0·102	14·6 : 20

The differences are slight, but they point to improvement, and show that the filtering and other purifying appliances of the Companies are in efficient order. It will be remembered that the May of last year was a very dry month, and in other respects the meteorological conditions were such as to conduce to a high purity of the river. The waters for the month just passed, while not quite reaching the same figures that were attained twelve months ago, are so nearly the same that for all practical purposes they may be considered to show the same degree of purity, the organic carbon being only 0·011 grain higher, whilst the oxygen required for the oxidation of the organic matter is only 0·004 grain per gallon higher.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.

METHODS OF ANALYSIS OF BUTTER.*

(Concluded from p. 284).

Estimation of Volatile Acids.

Reagents.

1. *Caustic Soda Solution.*—100 grms. of NaOH are dissolved in 100 c.c. of pure water. The caustic soda should be as free as possible from carbonates, and be preserved from contact with the air.

2. *Alcohol*, of about 95 per cent, re-distilled with caustic soda.

3. *Acid*, solution of sulphuric acid containing 25 c.c. of strongest H_2SO_4 in 1000 c.c. of water.

4. *Barium Hydrate.*—An accurately standardised, approximately decinormal solution of barium hydrate.

5. *Indicator.*—Alcoholic solution of phenolphthalein.

Apparatus.

1. *Saponification flasks*, 250 to 300 c.c. capacity, of hard well-annealed glass capable of resisting the tension of alcohol vapour at 100°.

2. *A pipette* graduated to deliver 40 c.c.

3. *Distilling apparatus.*

4. *Burette.*—An accurately calibrated burette reading to tenths of a c.c.

Manipulation.

Weighing the Fat.—The butter or fat to be examined should be melted and kept in a dry warm place at about 60° for two or three hours, until the moisture and curd have entirely settled out. The clean supernatant fat is poured off and filtered through a dry filter paper in a jacketed funnel containing boiling water. Should the filtered fat in a fused state not be perfectly clear, the treatment above mentioned must be repeated.

The saponification flasks are prepared by having them thoroughly washed with water, alcohol, and ether, wiped perfectly dry on the outside, and heated for one hour to boiling temperature. The flasks should then be placed in a tray by the side of the balance and covered with a silk handkerchief until they are perfectly cool. They must not be wiped with a silk handkerchief within fifteen or twenty minutes of the time they are weighed. The weight of the flasks having been accurately determined, they are charged with the melted fat in the following way:—

A pipette with a long stem, marked to deliver 5·75 c.c. is warmed to a temperature of about 50°. The fat having been poured back and forth once or twice into a dry beaker in order to thoroughly mix it, is taken up in the pipette, and the nozzle of the pipette carried to near the bottom of the flask, having been previously wiped to remove any adhering fat, and 5·75 c.c. of fat are allowed to flow into the flask. After the flasks have been charged in this way, they should be re-covered with the silk handkerchief and allowed to stand fifteen or twenty minutes, when they are again weighed.

The Saponification.—Ten c.c. of 95 per cent alcohol are added to the fat in the flask, and then 2 c.c. of the concentrated soda solution; a soft cork stopper is now inserted in the flask and tied down with a piece of twine. The saponification is then completed by placing the flask upon the water- or steam-bath. The flask during the saponification, which should last one hour, should be gently rotated from time to time, being careful not to project the soap for any distance up its sides. At the end of an hour the flask, after having been cooled to near the room temperature, is opened.

Removal of the Alcohol.—The stoppers having been laid loosely in the mouth of the flask, the alcohol is removed by dipping the flask into a steam-bath. The steam should cover the whole of the flask except the neck. After the alcohol is nearly removed, frothing may be noticed in

* Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (American) at its Meeting at Chicago, August, 1893.

the soap; and to avoid any loss from this cause or any creeping of the soap up the sides of the flask, it should be removed from the bath and shaken to and fro until the frothing disappears. The last traces of alcohol vapour may be removed from the flask by waving it briskly, mouth down, to and fro.

Dissolving the Soap.—After the removal of the alcohol the soap should be dissolved by adding 100 c.c. of recently boiled distilled water, warming on the steam-bath with occasional shaking, until solution of the soap is complete.

Setting Free the Fatty Acids.—When the soap solution has cooled to about 60° or 70° the fatty acids are separated by adding 40 c.c. of the dilute sulphuric acid solution mentioned above.

Melting the Fatty Acid Emulsion.—The flask should now be re-stoppered as in the first instance, and the fatty acid emulsion melted by replacing the flask on the steam bath. According to the nature of the fat examined, the time required for the fusion of the fatty acid emulsions may vary from a few minutes to several hours.

The Distillation.—After the fatty acids are completely melted, which can be determined by their forming a transparent oily layer on the surface of the water, the flask is cooled to room temperature, and a few pieces of pumice stone added. The pumice stone is prepared by throwing it, at a white heat, into distilled water, and keeping it under water until used. The flask is now connected with a glass condenser, slowly heated with a naked flame until ebullition begins, and then the distillation continued by regulating the flame in such a way as to collect 110 c.c. of the distillate in, as nearly as possible, thirty minutes. The distillate should be received in a flask accurately graduated at 110 c.c.

Titration of the Volatile Acids.—The 110 c.c. of distillate, after thorough mixing, are filtered through perfectly dry filter paper and collected in a flask graduated at 100 c.c. The 100 c.c. of the filtered distillate are poured into a beaker holding from 200 to 250 c.c., 0·5 c.c. phenolphthalein solution added, and decinormal barium hydrate run in until a red colour is produced. The contents of the beaker are then returned to the measuring flask to remove any acid remaining therein, poured again into the beaker, and the titration continued until the red colour produced remains apparently unchanged for two or three minutes. The number of cubic centimetres of the decinormal $Ba(OH)_2$ required should be increased by one-tenth.

Alternate Method of Determining Volatile Acids.

Saponification without the Use of Alcohol.—To avoid the danger of loss from the formation of ethers, and the trouble of removing the alcohol after saponification, the fat may be saponified with a solution of caustic potash in a closed flask without using alcohol. The operation is carried on exactly as indicated above for saponification in a closed flask, using caustic potash solution instead of soda, and omitting the operation for volatilising the alcohol. The caustic potash is prepared as follows:—Dissolve 100 grms. of the purest potassium hydrate in 58 grms. of hot dissolved water. Allow to cool in a stoppered vessel, decant the clear solution, and preserve in a vessel out of contact with the air. For the saponification use 2 c.c. of the caustic potash solution, which are poured on the fat after it has solidified in the flask. Great care must be taken that none of the fat is allowed to rise on the sides of the saponifying flask to a point where it cannot be reached by the alkali. During the process of saponification the flask can only be very gently rotated in order to avoid the difficulty mentioned. This process is not recommended in any except a closed flask with round bottom. In the subsequent solution of the soap use only 80 c.c. of distilled water, and in setting free the fatty acids use 60 c.c. of the dilute sulphuric acid. In other respects the distillation is conducted as previously described. Potash is used instead of soda, so as to form a softer soap, and thus allow a more perfect saponification.

The saponification may also be conducted as follows:—The alkali and fat in the melted state are shaken vigorously in the saponification flask until a complete emulsion is secured. The rest of the operation is then conducted as above.

Iodine Absorption Number.

Reagents.

1. *Iodine Solution.*—Dissolve 25 grms. of pure iodine in 500 c.c. of 95 per cent alcohol. Dissolve 30 grms. of mercuric chloride in 500 c.c. of 95 per cent alcohol. The last solution, if necessary, is filtered, and then the two solutions mixed. The mixed solution should be allowed to stand twelve hours before using.

2. *Decinormal Sodium Thiosulphate Solution.*—Take 24·6 grms. of chemically pure sodium thiosulphate freshly pulverised as finely as possible and dried between filter or blotting paper. Make this up to 1000 c.c. at the temperature at which the titrations are to be made.

3. *Starch Paste.*—One grm. of starch boiled in 200 c.c. of distilled water for ten minutes and cooled to room temperature.

4. *Solution of Potassium Iodide.*—150 grms. of potassium iodide dissolved in water and made up to 1 litre.

5. *Solution of Potassium Bichromate.*—Dissolve 3·874 grms. of chemically pure potassium bichromate in distilled water and make the volume up to 1 litre at the temperature at which the titrations are to be made.

Manipulation.

Standardising the Sodium Thiosulphate Solution.—Run 20 c.c. of the potassium bichromate solution, to which has been added 10 c.c. of the solution of potassium iodide, into a glass-stoppered flask. Add to this 5 c.c. of strong hydrochloric acid. Allow the solution of sodium thiosulphate to flow slowly into the flask until the yellow colour of the liquid has almost disappeared. Add a few drops of the starch paste, and with constant shaking continue to add the sodium thiosulphate solution until the blue colour just disappears. The number of c.c. of thiosulphate solution used multiplied by 5 is equivalent to 1 grm. of iodine.

Example.—20 c.c. $K_2Cr_2O_7$ solution required 16·2 c.c. sodium thiosulphate; then $16·2 \times 5 = 81$ = number c.c. of thiosulphate solution equivalent to 1 grm. of iodine. Then 1 c.c. thiosulphate solution = 0·0124 grm. of iodine. Theory for decinormal solution of sodium thiosulphate, 1 c.c. = 0·0127 grm. of iodine.

Weighing the Sample.—About 1 grm. of butter fat is to be weighed in a glass-stoppered flask holding about 300 c.c., with the precautions mentioned for weighing the fat for determining volatile acids.

Absorption of Iodine.—The fat in the flask is dissolved in 10 c.c. of chloroform. After complete solution has taken place, 30 c.c. of the iodine-mercuric chloride solution is added. The flask is now placed in a dark place and allowed to stand, with occasional shaking, for three hours.

Titration of the Unabsorbed Iodine.—100 c.c. of distilled water are added to the contents of the flask, together with 20 c.c. of the potassium iodide solution. Any iodine which may be noticed upon the stopper of the flask should be washed back into the flask with the potassium iodide solution. The excess of iodine is now taken up with the sodium thiosulphate solution, which is run in gradually, with constant shaking, until the yellow colour of the solution has almost disappeared. A few drops of starch paste are then added, and the titration continued until the blue colour has entirely disappeared. Toward the end of the reaction the flask should be stoppered and violently shaken, so that any iodine remaining in solution in the chloroform may be taken up by the potassium iodide solution in the water. A sufficient quantity of sodium thiosulphate solution should be added to prevent a re-appearance of any blue colour in the flask for five minutes.

Setting the Value of the Iodine Solution by the Thiosulphate Solution.—At the time of adding the iodine solution to the fats, two blank flasks of the same size as those used for the determination should be employed for conducting the operation described above, but without the presence of any fat. In every other respect the performance of the blank experiments should be just as described. These blank experiments must be made each time the iodine solution is used.

Example.—Blank Determinations.

1. 30 c.c. iodine solution required 46·4 c.c. sodium thiosulphate solution.
2. 30 c.c. iodine solution required 46·8 c.c. of sodium thiosulphate solution.

Mean, 46·6.

Per Cent of Iodine Absorbed.

Weight of fat taken	1·0479	grms.
Quantity of iodine solution used	0·30	c.c.
Thiosulphate equivalent to iodine used..	46·6	,,
Thiosulphate equivalent to remaining iodine	14·7	,,
Thiosulphate equivalent to iodine absorbed	31·9	,,

Per cent of iodine absorbed, $31·9 \times 0·0124 \times 100 \div 1·0479 = 37·75$.

ON THE ORIGIN OF GOLD NUGGETS.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

(Continued from p. 283).

The preceding experiments are not numbered because they are merely qualitative ones, but the next series of experiments were quantitative; weighed pieces of pure sheet-gold were put up with various organic reducing substances; sulphides and other naturally occurring substances which I thought might form a galvanic couple, and which would throw down the gold from solution upon the plate as in the electroplating process.

A.—*With a Gold Nucleus and Organic Matter.*

In the following experiments pure gold specially prepared by the late Dr. Leibius, Senior Assayer of the Sydney Mint, and assaying 1000, was rolled out into fillets of $\frac{1}{100}$ inch thick, so as to expose a large surface and yet be strong enough to handle; these were heated in a cornet crucible to burn off impurities and then boiled with nitric acid, and well washed to get rid of any sulphur or other contaminations from the gas flame. The nuggets and specimens of native gold used as nuclei were also cleaned in the same way. The fillets were next weighed and placed in stoppered glass cylinders with a solution of the sodium chloraurate, supplied for photographic purposes, and made up of the usual strength of a fifteen grain tube of the salt to fifteen ounces of water.

The reducing substances were similar to those used by Wilkinson, but, as will be seen, with results just the reverse of what he obtained, *i.e.*, the gold foil or other nucleus weighed less instead of more after the experiments.

Expt. 1.—A water-worn nugget was used as a nucleus, the dust of the air was allowed to fall in, and the experiment was continued for 168 days, with an occasional addition of gold solution as the liquid in the cylinder became colourless from the reduction of the gold. Although a good deal of gold was precipitated on and around the nugget, none of it was adherent, and on re-weighing it was found to have lost 0·002 grm.

Expts. 2 *and* 3.—A plate of pure gold was used as a nucleus in each case, and the solution was exposed to the air as above; one plate lost 0·0042 and the other 0·0038 grm.

Expt. 4, *with Cork.*—The gold solution was left in a stoppered cylinder with a slice of clean new cork until the yellow colour of the solution had disappeared, showing that all the gold had been removed from it. Some gold was precipitated at the bottom of the cylinder, some on the sides, and a little floated as films on the top; there was also a small quantity of gold precipitated on the gold plate, but this was non-adherent and came away on washing the plate in a jet of water. This plate underwent no change in weight.

Note.—All of my experiments were carried out in full daylight, and not in the dark like those by Wilkinson, Egleston, and others.

Expt. 5, *with Swedish Filter-paper.*—The yellow colour soon disappeared from the solution, and the paper acquired a purple colour. The gold plate lost 0·0036 grm. in weight.

Expt. 6, *with Phosphorus in Ether.*—The solution soon became colourless, and a black precipitate of gold was thrown down on the bottom of the cylinder and on the gold plate. Floating films of gold also formed on the surface. On washing the gold plate with a jet of water, all the gold deposited on it was washed away, and on drying and weighing it was found to have lost 0·0004 grm.

Expt. 7.—In this case a freshly-broken jagged fragment of gold in quartz was used as the nucleus instead of a gold plate, but cleaned with the same care. Cuttings from a cedar pencil and some scraps of paper were added; these acted in the same way as the cork, and were "mineralised" by the reduced gold; the gold and quartz nucleus lost 0·0021 grm. in weight.

Expt. 8.—Paper and wood were used as in Experiment 7, with a nucleus of jagged gold set free from quartz by means of hydrofluoric acid; the nucleus lost 0·0013 grm.

Expt. 9.—Similar to experiment 8, with a nucleus of native gold from Sandhurst (Bendigo). This showed a loss of 0·0001 grm.

On incinerating the cork, cedar, &c., which had been used for reducing the gold, the residue retained the original form, but much shrunken; and as has been observed by others, the microscopic structure of a cut section presents the appearance of burnished gold from the pressure of the knife.

The experiments in Table all show that instead of the nucleus or nugget of gold increasing in weight and size in the presence of organic matter, there is a decrease which is just the reverse of the effects obtained by Wilkinson, Daintree, and others.

The loss in weight of the nucleus may have been due to the removal of small quantities of impurity in the gold used as a nucleus; the native gold would of course contain silver and other impurities, but the gold foil was regarded as particularly pure by the late Dr. Leibius, of the Sydney Mint, by whom it had been assayed. This will be the subject of further experiment; the point of chief interest at this stage is that the nuclei did not show any increase in weight.

B.—*With a Gold Nucleus and Inorganic Matter.*

Experiments from Nos. 10 to 49 form the third series, in which a galvanic couple was formed.

Expt. 10, *with Molybdenite.*—No gold was visible on the molybdenite, but on closer examination some was seen between the cleavage planes of the mineral, and this under the microscope had a vermicular and matted structure. On removing the gold plate and cleaning with a brush, it was found to have increased 0·0038 grm. in two months.

Expt. 11, *with Mispickel.*—The solution was decolourised in twenty-four hours, and this went on continuously

* A Paper read before the Royal Society of New South Wales, September 6, 1893.

No.	Nucleus.	Reducing matter.	Original weight of nucleus.	Weight of nucleus after experiment.	Difference in grms.	Number of days.
1.	Nugget.	Dust from air.	3·4920	3·4900	−0·0020	168
2.	Gold foil.	,, ,,	1·5152	1·5110	−0·0042	168
3.	,,	,, ,,	1·1713	1·1675	−0·0038	168
4.	,,	With cork.	1·1410	1·1410	none	273
5.	,,	With filter-paper	0·8500	0·8464	−0·0036	273
6.	,,	Phosphorus in ether.	0·9330	0·9326	−0·0004	273
7.	Gold in quartz.	Paper and wood.	1·7630	1·7609	−0·0021	58
8.	Gold from quartz.	,, ,,	2·8487	2·8474	−0·0013	58
9.	,, ,,	,, ,,	0·6574	0·6573	−0·0001	58

for many successive days. Increase in weight in fifty-nine days 0·0006 grm.

Expt. 12, *with Mispickel.*—The gold foil was stained nearly black on both sides over about two-thirds its area; the black deposit had a blistered or mammillated structure, very marked under the microscope and readily felt with the finger-nail. It increased 0·0260 grm. in fifty-nine days. The gold on the mispickel was also dull and mammillated, but in part showed traces of cubes joined in strings, and in one place there were hexagonal plates (microscopic) of bright lustrous gold.

Expt. 13, *with Mispickel.*—The gold deposited on the mispickel was black and pulverulent, and without crystals. The gold on the gold foil was of a bronze-green tint. The plate increased 0·0089 grm. in weight in nine days.

Expt. 14, *with Recent Iron Pyrites, Loffley's, Taupo.*—Contained a very large quantity of ferrous sulphate and sulphuric acid; probably none of the pyrites left unoxidised. It reduced a very large quantity of the gold solution, but none was permanently deposited on the plate, and the weight remained unchanged. On dissolving out with hydrochloric acid, a residue of spongy gold was left, together with some particles of a white mineral, probably silica, as the springs at Loffley's deposit this mineral.

Expt. 15, *with Cubical Iron Pyrites.*—Decolourised in twenty-four hours. The gold foil or plate was dull from the gold which had been deposited upon it. Increase in weight 0·0028 grm. in fifty-nine days.

Expt. 16, *with Pyrites, Joshua's Spa, Lake Taupo, N.Z.*—Several charges of gold solution were reduced. The foil was blackened, and a black powder came away on rubbing with the finger, but some permanent brown-coloured gold was left on the foil. The foil increased 0·0060 grm. in weight in fifty-nine days.

A certain amount of loose gold was thrown down with some of the minerals, but no account was taken of this, as the chief object was to ascertain whether a nucleus of gold would have a coherent film of gold deposited upon it when the nucleus formed one element of a couple; and this was found to be the case. The deposit of gold on the foil was usually of a dull reddish brown colour, felt rough to the nail, and under the microscope was seen to be mammillated, and when rubbed with a hard substance like agate or a glass rod, presented a series of bright points.

Expt. 17, *with Iron Pyrites.*—Part of an uncrystallised mass. The coating of gold was dull, with here and there a bright speck, something like the hexagonal plates on the copper pyrites, but the outlines rather irregular; bright gold also along the cracks in the pyrites. The deposit on the plate was of a full copper colour, very rough, and weighed 0·0708 grm.

Expt. 18, *with Iron Pyrites.*—Part of a pentagonal dodecahedron acquired a dull brown deposit of gold, but no crystals were detected. A similar brown film on the plate increased 0·0633 grm. in weight.

Expt. 19, *with Rhombic Iron Pyrites or Marcasite.*—Became coated with dull brown gold, which gave it the appearance of a coating of rust; there were a few bright specks, but no distinct crystals of gold. The gold plates acquired a bronze colour with a greenish shade, became rough, and increased 0·0328 grm. in weight.

Expt. 20, *with Brown Hæmatite.*—Decolourised several charges. Foil became dull and increased 0·0003 grm. weight in fifty-nine days.

Expt. 21, *with Limonite.*—Decolourised seven ounces of the gold solution. Foil became dull and increased 0·00025 grm. in weight in fifty-nine days. The deposited gold was dull and mammillated.

Expt 22, *with Rust.*—A mixture of black and brown oxides from old sheet iron. The gold foil became very dull and dirty looking. Increased 0·0011 grm. in fifty-nine days. On dissolving the residue in hydrochloric acid, only dark coloured spongy gold was left.

Expt. 23, *with Yellow Copper Pyrites.*—After fifteen days the gold plate was dull from deposited gold. Increase in weight 0·0059 grm. in fifty-nine days.

Expt. 24, *with Copper Pyrites.*—Reduced several charges of the gold solution. The foil became deeply stained, and acquired a rough appearance and feel, of the usual brown colour; under the microscope it was seen to be much mammillated, and increased 0·0185 grm. in weight in fifty-nine days. A large amount of gold was also thrown down on the pyrites, which under the microscope was seen to have a matted vermiform appearance; a certain amount of loose powdery gold was also precipitated.

Expt. 25, *with Copper Pyrites, Walleroo, S.A.*—The deposit of gold was almost black, but mixed with it were a few very bright microscopic hexagonal plates of gold. The deposit of gold on the plate was very rough and almost black in places, and it had increased in weight 0·0666 grm.

Expt. 26, *with Redruthite (Copper Sub-sulphide).*—The gold was deposited on the sulphide as a black powder, with a little dull yellow in parts. The gold plate became of a dull brown colour near where it had been in contact with the mineral; the upper part was merely stained. Increase = 0·0836 grm.

Expt. 27, *with Silver Sulphide (Argentite).* No change for some time, but between June 28 and November 30 it reduced five ounces of the gold solution and became coated with gold. Some of the gold was crystallised in microscopic imperfect hexagonal scales. The gold plate increased 0·0083 grm. in 155 days.

Expt. 28, *with Fused Artificial Silver Sulphide.*—The gold deposited upon it was vermiform, and a thin coating of dead gold formed on the plate, which increased 0·0082 grm. in weight in nine days only.

Expt. 29, *with Galena.*—The cleavage planes became gilt almost immediately, *i.e.*, in a minute or so; without the gold nucleus the gilding takes an hour or two. As the deposit of gold thickens it loses its brilliancy. After a fifteen-days action the gold plate had become dull from the gold deposited upon it. Increase 0·0049 in fifty-nine days.

Expt. 30, *with Galena, Broken Hill, N.S.W.*—The gold deposited on the galena was black, but brown in places, with a few rectangular specks of bright gold; some lead sulphate had also formed. The gold on the gold plate was of a copper colour. The foil increased 0·0281 grm. in weight.

Expt. 31, *with Zinc Blende.*—Decolourised several charges. The foil was unchanged. On dissolving the blende, much dull spongy gold was left mixed with a few bright crystallised points seated on the gold; one St.

Andrew's cross was very distinct, also some with six rays, but all microscopic.

Expt 32, *with Zinc Blende.*—Increase in weight of plate was 0·0086 grm. Mixed with the dull vermicular gold on the blende were scattered hexagonal crystals of bright gold.

By vermicular or vermiform gold is meant a more or less close net-work of worm-like rounded and irregular threads of gold, which eventually coalesce in the thicker deposits and form a mammillated surface.

Expt. 33, *with Graphitic Casing from an Auriferous Vein.*—It decolourised two ounces of the solution in five days and successive quantities afterwards. The surface of the graphitic casing became completely coated with a very thick deposit of dark coloured mammillary gold, but in a few places were some minute crystals of bright gold showing up most brilliantly; they appeared to be hexagonal plates. The gold foil did not show any increase in weight.

In this instance, as well as in that of the coal, graphite, and charcoal, the gold appeared to be thrown down entirely upon the precipitants, and none came down as a loose powder nor upon the sides of the glass vessel. The miners of Ballarat and other places attach a good deal of importance to the graphite basing of veins, and speak of it as the "indicator." It usually contains iron pyrites; the carbon and pyrites together reduce the gold very quickly.

Plates of pure gold, cleaned by ignition and boiling potash, were also placed in photographer's gold solution with the following non-metallic substances; they were shaken daily and re-filled with fresh gold and sodium chloride solution as often as the solution became colourless.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, June 8th, 1894.

Prof. A. W. RÜCKER, M.A., F.R.S., President, in the Chair.

PROF. RAMSAY, in opening the discussion on "*Experiments on the Relations of Pressure, Volume, and Temperature of Rarefied Gases,*" by Mr. E. C. C. BALY and himself, recapitulated the chief points in the paper.

Siljeström in 1873 and Mendeleeff in 1875, he said, had both found that gases become less compressible than Boyle's law would give as rarefaction proceeds. Amagat in 1883 examined the subject, and concluded it was impossible to make measurements sufficiently accurate to decide the question one way or the other. In 1886 Bohr investigated the compressibility of oxygen, and found its behaviour abnormal about 0·7 m.m. pressure. Van der Wen's experiments (1889) led him to conclusions opposite to those of Siljeström and Mendeleeff, and those of Melander (1892) gave support to Van der Wen's results. To decide the question at issue the authors took up the subject, and their results confirm the conclusions of Siljeström and Mendeleeff. They also prove that oxygen behaves abnormally about 0·75 m.m. as found by Bohr.

Prof. PERRY said some of the terms used in the paper required alteration. The word "elasticity" was employed in several senses, sometimes being used to denote "$p\,v$," the product of pressure and volume, whilst at others its ordinary meaning was intended. He did not quite understand the connection between $p\,v$ and the thermal expansion to which the authors refer at the end of their paper. Taking Ostwald's equation for gases $(p+a)\,v = R\,t$, he proceeded to show that the coefficient of expansion would be constant whether $p\,v$ was constant or not.

Dr. BURTON said he had been accustomed to think as pressure was reduced gases approached the simple or "perfect" state. It was very desirable that similar experiments be made on other gases to ascertain if any had constant coefficients of expansion. He failed to see why the internal energy should increase as the pressure decreases, unless under these conditions energy travels more by radiation than by conduction or convection.

The PRESIDENT, speaking of the adhesion of gases to the surface of glass, suggested experiments on the effects produced by varying the ratio of the surface to the volume of the gas. On the subject of distribution of energy he was inclined to agree with Dr. Burton's view rather than with the authors' suggestion. One would not be led by *a priori* reasoning to expect that the internal energy would increase with decrease of pressure.

Prof. RAMSAY, in reply, said that in the experiments on oxygen at about 0·75 m.m. pressure the greater part of the gas was sometimes found in one McLeod gauge and sometimes in the other. Only after standing seventy-eight hours did the quantities trapped in the two gauges become equal. The only explanation they could think of was that the temperatures of the gauges might not have been absolutely the same. Speaking of the suggested increase of internal energy with decrease of pressure, he said Prof. Dewar's experiments tend to show that there was little conduction through vacuous spaces.

The PRESIDENT thought Dr. Bottomley's researches had shown that radiation also falls off rapidly as the pressures become very small.

Owing to the absence of Capt. Abney, the Exhibition of Photographs of Flames which had been announced was postponed.

A paper on "*The Isothermals of Ether*" was read by Mr. ROSE INNES.

Taking the important linear law $p = b\,T - a$, connecting the pressure and temperature of substances (liquid and gaseous) at constant volume, given by Ramsay and Young (*Phil. Mag.*, xxiii., p. 436) and subsequently confirmed by Amagat and Tait, the author has endeavoured to express the constants b and a in terms of the volume v. Using the results of Ramsay and Young's experiments on ether, because they extended over a large range of volume (1·9 to 300), the following formulæ were found to give the best approximation, viz.,—

$$b = \frac{751{\cdot}9}{v - 0{\cdot}9173\,v^{\frac{2}{3}}} \text{ and } a = \frac{23{,}300{,}000}{v^2 + 11{\cdot}05\,v^{\frac{4}{3}}}$$

Tables and curves accompany the paper, showing that for volumes between 6 and 300 the agreement of calculated and observed values of p do not differ more than can be accounted for by errors of experiment. For volumes less than 5 the formula for p gives numbers quite wrong. In searching for a physical basis for the expressions for b and a, the author puts l^3 for v in the above formulæ, l being the side of a cube whose volume is v. The expression for p then becomes—

$$p = \frac{R\,T}{l^3 - c\,l^2} - \frac{A}{l^6 + k\,l^4} \quad .. \quad .. \quad .. \quad (3)$$

Writing the coefficient of T in the form—

$$\frac{R}{l^3} \cdot \frac{l}{l-c}$$

the author goes on to show that this form might be expected if the molecules had finite dimensions, for the number of impacts on the faces of a cube would be increased in the ratio—

$$\frac{l}{l-c},$$

where c is a quantity depending on the size of the molecules. Ingenious arguments suggested by Van der Waals' remark that his formula must not be pushed beyond the point where the actual volume is less than eight times the volume of the molecules lead the author to infer that

for ether this limiting volume is somewhat above 6. Hence he would not expect his (Mr. Rose Innes) formula to hold below this volume. The formula for *a*, the "internal pressure," is explained on the supposition that a "skin" effect exists between the matter in the vessel and the boundary layers. By clearing expression (3) of fractions the author shows that the shape of the isothermals is represented by an equation of the 7th degree in *l*, which cannot have more than three positive roots, and thence infers that isothermals are not necessarily represented by cubic equations as is sometimes assumed.

Prof. RAMSAY said Mr. Rose Innes's formula was much more satisfactory than that of Van der Waals, which was at best only a rough approximation.

The PRESIDENT objected to the use made of the word "discontinuity" in the paper as being quite different to its precise mathematical meaning. He also pointed out that the author's argument respecting the effect of finite molecular dimensions was much less general than that of Van der Waals. Although the new formula agreed with experiment over a longer range of volume than that of Van der Waals, it would not be safe to argue beyond the range of the experiments it represented.

NOTICES OF BOOKS.

Micro-Organisms in Water: their Significance, Identification, and Removal. Together with an Account of the Bacteriological Methods employed in their Investigation. Specially Designed for the Use of those connected with the Sanitary Aspects of Water Supply. By PERCY FRANKLAND, Ph.D., B.Sc., F.R.S., F.C.S., F.I.C., &c., and Mrs. PERCY FRANKLAND (joint Author of "Studies on some New Micro-organisms obtained from Air, &c."). London and New York: Longmans, Green, and Co. 1894. 8vo., pp. 532.

RARELY, if ever, have we had the good fortune of meeting a more valuable contribution to sanitary science. The authors have collated the most important results obtained in bacteriological practice. They hope, with good grounds, that their work may be serviceable not only to the student and investigator, but "to those who, like *engineers* and medical officers of health, are practically concerned with the hygienic aspects of water supply." We interrupt ourselves here to ask whether "technical chemists" would not have been an appropriate substitute for engineers. An engineer, whether civil or military, is *as such* no more qualified to deal with the hygienic aspects of water supply than would be a barrister or a clergyman.

The authors commence their work with instructions on sterilisation and the preparation of culture media. They describe sterilisation by steam, by hot air, by filtration, and by chemical agents. Among the filters, those only of Chamberland and of Berkefeld (baked infusorial earth) deserve and receive notice, though gases may be freed from micro-organisms by a passage through sterile cotton-wool.

Culture media, solid and liquid, are described with praiseworthy fulness and accuracy, as are also the methods for the isolation of the various micro-organisms. We have Jörgenson's hæmatometer, gelatin plate culture, the Petri culture dish, the Esmarch tube culture, and Fränkel's anærobic tube culture.

In the second chapter the reader is introduced to the staining and microscopic examination of micro-organisms. The solutions specially described are those of Löffler, Weigert, Ehrlich, Ziehl, Gram, and Gram-Günther. For the Gram process it is pointed out that only the pararosaniline products are available; magenta, methylene-blue, and Bismarck brown being useless. Cover-glass preparations, the staining of spores, double straining, the straining of flagella and drop cultures are next described in a manner which shows the thorough familiarity of the writers with their subjects.

In the third chapter we come to the examination of water for microbia, especially the collection of samples. An instrument is figured (Miquel's) for obtaining such samples at known depths. As regards the special culture media employed, it is shown that in the comparative examination of waters by different observers an accurate determination of the alkalinity of the gelatin peptone employed should be effected. The bacteriological examination of waters used in brewing is expounded at some length, but we find no observations bearing on its probable utility in connection with the tinctorial industries. The discrepant results obtained at different dye, print, and colour works do not all seem to admit of explanation by the chemical composition of the waters.

The numerical determination of bacteria is given by the methods of Miquel and Wolffhügel is explained, as also the photographic reproduction of a gelatin plate culture.

In Chapter IV. the authors compare the bacteria contents of various waters. The general public are little aware that the purest ice, and even distilled water if not recently prepared, are not free from bacteria. In ice stored by a company at Berlin the bacteria varied from 21 to 8800 per c.c. The waters of the Lea and the Thames are most contaminated with microbia in winter, as are also those of the Seine, the Marne, and the Ourcq. The river Dee (Scotland), it is said, "affords a most perfect example of the repeated pollution and the repeated restoration of a stream to a state of comparative bacterial purity" (p. 101). Hygienic chemists are duly cautioned that "in the examination of well-water for micro-organisms due attention should be paid to the conditions recently prevailing, *e.g.*, as to whether the well has been recently pumped or disturbed, or has been unused for a longer or shorter period; and unless these circumstances are duly taken into consideration, the most misleading and erroneous conclusions will be arrived at."

The distribution of micro-organisms in sea-water, at different distances from land and at different depths, is a point of no small interest.

The fifth chapter takes up the most important point, the purification of water for drinking purposes. A distinction is drawn between different kinds of pollution. In case of excessive vegetable contamination, chemical treatment is indicated; whilst in waters which have received sewage impurities, the reduction of the organisms present takes the first place. Sand filtration is of comparatively small avail for the removal of lifeless organic impurities, though it takes a higher position if judged by bacteriological methods. The comparative mortality from cholera at Hamburg and Altona in 1892 seems to show the difference between good filtration and its absence. Garden soil and peat have proved themselves very efficient media for the filtration of sewage, as far as the retention of microbia is concerned, but the rate of filtration is so slow as to render them both practically useless. At the point where the irrigation waters from Gennevilliers enter the Seine the number of bacteria rises to above 200,000 per c.c.

For domestic filters the authors give the preference to the Chamberland (unglazed porcelain) and the Berkefeld (baked kiesel-guhr). The latter has the advantage in the rate of filtration, whilst it is equally efficacious in keeping back bacteria. Stone filters have been found untrustworthy. Water may be purified by a temperature of 100° kept up for fifteen minutes; the most dangerous pathogenic forms, such as the germs of cholera and typhoid, being thus eliminated. Sedimentation is an important means for the purification of water on the large scale. Alumina is more efficient than lime. We can decidedly confirm the statement that "in precipitation by ferric sulphate and crude alum (better, aluminium sulphate) the addition of lime was found to be unnecessary." The attempt to purify a rich sewage by intermittent filtration through sand, we have repeatedly found eventuates in choking up the filter-beds. The sewage experimented on by the Massachusetts State Board of Health was exceedingly weak. The

use of lime, except mineral acids or strong solutions of acid salts are present, we have always found not merely useless, but detrimental.

From the chapter on the detection of pathogenic bacteria in water, we find that polluted waters are dangerous, not merely for drinking, but for bathing.

Special methods, *e.g.*, those of Uffelmann (of Holz), Parietti, Vincent, and others, are then given for the detection of the typhoid bacillus. The detection of Koch's comma bacillus is next given according to Schollelius, Vestea, Löffler, and others.

The vitality of typhoid, cholera, anthrax, and other pathogenic bacteria in different waters is given in the form of tables.

The action of light upon micro-organisms in water and culture media is made the subject of a special chapter. It may be safely said that to cover in filter-beds and precipitation and subsidence tanks from the light is a grave error.

The Appendix is not the least valuable feature of this excellent work. It begins with the forms of bacteria magnified to about 700 diameters. Under each species we find its action upon gelatin, the authority for details, its locality, its microscopic appearance, its cultures, and remarks on its pathological action. The names of the unquestionably pathogenic species are printed in red type.

This is a book which should be at once added to the library of every municipal board, sanitary official, and consulting chemist throughout the realm.

The Unity of the Chemical Elements. ("Der Monismus der Chemischen Elemente"). By Dr. Edouard Meusel. Liegnitz: Scholz. 1893.

We salute this little work as the utterance of a man who seeks in chemistry for something higher than mere *Lagerungs formel* and sesquipedalian nomenclature. The author, however, by no means ignores the possible applications of the chemistry of the future, since he rightly declares that the welfare of mankind must be aimed at, not by political and social "demonstrations" and movements, but by an increased power over matter. Whether this increased power is to be sought for in the way of the synthesis of food products, or of control over the weather, or of the destruction of creatures which compete with us for the use of nutritive substances, is left, for the present, an open question.

Dr. Meusel openly admits his conviction that our present seventy-five elements are all formed from one primitive matter.

He places as a motto on his title page the declaration of Delisle that "chemical research culminates in the question of the nature and the origin of the elements."

He seeks to show that "the atoms of the various elements have arisen only by different condensation, by dissimilar occupation of space, and unequal quantitative accumulation." He duly appreciates the value of the steps hitherto taken in this direction, such as the atomic theory of Dalton, the hypothesis of Prout, and the periodic system as presented by Newlands, Mendeleeff, Meyer, and Crookes, whose arrangements he quotes. But he objects that, while some properties of the elements are in harmony with such systems, others, such as the atomic volumes and the thermochemical behaviour of the elements, fully show the complete insufficiency of the periodic system.

We must here remark that while Crookes upholds the origin of our elements from one primitive matter—protyle—Mendeleeff regards the elements as radically and essentially distinct.

Dr. Meusel, however, proclaims that his task in the work before us is to convert the words of Crookes into fact. He attempts to find the numbers which may be used in the construction of the atomic weights from the differences of the initial numbers of the several series, *i.e.*, from the atomic weights of Li, G, B, C, N, O, and Fe. The components of these seven initial members are the values 3·99 and 3·02. The atomic weights for each of the elements are obtained by combining 3·99 and 3·02, or their multiples. He admits that in nearly every case a small value must be subtracted from the sum of the components in order to arrive at the atomic weights as determined by experiment. This, however, he does not regard as a valid objection. He regards these discrepancies as an internal necessity.

His next task is to arrive at a common origin for the magnitudes 1·00 (H) with the two magnitudes 3·99 and 3·02, and if possible to arrive at a clear view of the special relations of these magnitudes.

He therefore constructed the simplest system of atoms moving in common. The simplest figures, tetrahedra, and spheres, are determined by four given points in space. The four corners of a tetrahedron, if replaced by four atoms, form the initial point for the author's further deductions, shown by diagrams.

For a cosmic system there are required elements which can resist both extremely high and low temperatures and pressures. For millions of years they were created out of the primal matter, for which elements readily decomposable were not adapted.

The principle of substitution which has served for building up the atom of hydrogen in which an angle of the tetrahedron was replaced by an atom of the new tetrahedron has been applied by infinite Wisdom for arranging and enlarging the hydrogen. In this principle of substitution lies the basis for the creation of the cosmic bodies, the base for the possibility of the existence of living beings.

He calculates for hydrogen the weight of a single particle (molecule?) 0·000000000000000000000004 grm. An atom of the primal material, therefore, would weigh the 200th part of this amount.

In the next section, Dr. E. Meusel shows the composition of the chemical elements on his system. He next discusses in full valency as an evidence of the unity of the elements.

He then proceeds to the atomic volume as a proof of the unity of the chemical elements. Next follow the thermochemical proofs, with the remark that the section affords to chemistry that which Newton in his day gave to astronomy by his law of gravitation. He regrets that space does not allow him to add studies on the connection of atomic composition with crystallisation, with magnetism, and with the electric phenomena.

In summing up, the author enquires were men like Moleschott and Büchner justified by the amount of their knowledge in making an onslaught on any consideration of the world?

"The man who can effect chemical precipitations or coloured reactions, produces artificially some chemical compound, may perhaps close his ears to the all-wise Spirit of Creation; but he who can recognise in the quadrillionth part of a c.c. of matter how the plan of creation comes in evidence, certainly feels himself penetrated by the omnipresence of this incomprehensible Spirit. It is the greatest error of certain religious teachers to reject everything derived from nature, and to leave the works of the Almighty Creator to be interpreted by those whose interest is a war against religion."

To all truly philosophic chemists, Dr. Meusel's work will prove a most valuable and suggestive study.

The History of Hydrotimetry.—Prof. Dr. L. L. de Koninck points out in the *Chemiker Zeitung* that Dr. Clark, in his process for determining the hardness of water, had been anticipated by Accum in his "Practical Treatise on the Use and Application of Chemical Tests, &c." (1818, Second edition). Clark's merit, according to de Koninck, consists in his having rendered the process quantitative by an adoption of the volumetric method.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 23, June 4, 1894.

Dr. d'Arsonval was elected a member of the Section of Medicine and Surgery *vice* the late Dr. Brown-Sequard. His election will be in the usual course submitted for ratification to the President of the Republic.

Composition of Apophyllite.—C. Friedel.—The analytical results are fairly well represented by the formula $4Si_2O_7,CaH_4+KOH$.

New Researches on the Chloroboracites. — G. Rousseau and H. Allaire.—Boracite constitutes a chemical type in which the magnesium may be replaced by various metals, and bromine, iodine, and fluorine may be substituted for chlorine. These compounds have been obtained by causing metallic chlorides in the state of vapour to react upon boronatrocalcite. The authors have formed and described the corresponding zinc, cadmium, nickel, cobalt, manganese, and magnesium compounds.

The Rôle of the Transformations of Iron and Carbon in the Phenomenon of Tempering.—Georges Charpy.—Tempering, among other modifications, occasions a transformation of the iron (shown by the traction test) and a transformation of the carbon (characterised by the method of Eggertz). The former modification seems to have merely a very slight influence on the breaking load, whilst the transformation of carbon seems a correlative of the increase of hardness.

A Bromocupric Hydrobromate and a Red Cupropotassium Bromide.—Paul Sabatier.—The former of these compounds seems to have the composition—

$$3CuBr_2,2HBr,6H_2,$$

though the instability of the substance, already in a state of partial dissociation, leads us to ascribe to it the formula $CuBr_2,HBr,2H_2O$. The red double bromide is anhydrous, and is represented by the formula $CuBr_2KBr$.

Analytical Separation of Chlorine and Bromine.—R. Engel.—This paper will be inserted in full.

Detection of Hydrobromic Acid.—A. Villiers and M. Fayolle.—This memoir will also be inserted *in extenso*.

New Derivatives of the Cyanacetic and Cyanosuccinic Ethers.—L. Barthe.—The author examines firstly the action of ethyl mobromopropionate upon sodium-ethyl cyanacetate, obtaining cyanoglutaric acid. He further obtains dimethylcyanosuccinic ether by the action of bromoisobutyric ether upon sodium-ethyl cyanacetate. He has also studied the action of monobromosuccinic ether upon sodium-ethyl cyanosuccinate, the saponification of ethyl β-cyanotricarballylic acid and methyl tricarballylate.

Combinations of Pyridine with the Permanganates.—T. Klobb.—The author has obtained a series of compounds of pyridine and the silver, copper, zinc, and nickel permanganates parallel to the ammonium compounds.

The Emetics.—Paul Adam.—(French chemists use the term "emetic," irrespective of physiological action, to include all compounds analogous in constitution to the well-known "tartar emetic"). The theories put forward concerning the constitution of the emetics may be reduced to two: do antimonious hydrate, ferric hydrate, and boric acid act in these salts as acids or as bases? The classic formulæ correspond to the second theory, whilst the researches of Jungfleisch favour the former and are supported by the present author. He concludes that the chemical analogies and reactions of "emetic," properly so-called, should make us regard substances of this kind as ether salts and not as double salts.

Monoethylphosphoric Acid.— J. Cavalier.—Monoethylphosphoric acid, $PO_4C_2H_5H_2$, obtained by Pelouze, yields a series of salts of the formula $PO_4C_2H_5M_3$, which have been prepared by Pelouze and Church. This acid presents two clearly distinct acid functions and yields two series of definite salts, corresponding to the formulæ—

$$PO_4C_2H_5MH \text{ and } PO_4C_2H_5M_2.$$

Action of Trioxymethylene upon Alcohols in presence of Ferric Chloride, and on the New Methylsnic Derivatives thence resulting.—A. Trillat and R. Cambier.—The authors' method consists in causing trioxymethylene to react upon alcohol in presence of a small quantity of ferric chloride. The reaction ensues according to the general formula—

$$(CH_2O)_3 + 6ROH = 3.CH_2(OR)_2 + 3H_2O.$$

The ingredients are mixed in equimolecular proportions, and heated with a proportion of ferric chloride varying from 1 to 4 per cent. Heat is applied for from two to ten hours. The authors have verified this method upon the saturated alcohols of the fatty series, upon the non-saturated alcohols, and on the plurivalent alcohols.

Mechanism of the Action of Chlorine upon Isobutylic Alcohol. — A. Brochet. — This paper is not adapted for useful abstraction.

Red Pigment of Pyrrocoris Apterus.—C. Phisalix. —The ease with which we can collect large quantities of this hemipteron led me to attempt the isolation and examination of the red colouring matter of its integuments. Two litres of the insects freshly caught were desiccated *in vacuo*, and the matter was then treated with carbon disulphide. All the fatty matter was dissolved, and at the same time the colouring matter which gave the liquid a gooseberry-red colour. Alcohol and petroleum dissolve a yellowish colouring matter. These solutions present an absorption-spectrum closely resembling that of carotine, and the residue from their evaporation, on treatment with concentrated sulphuric acid, took a greenish blue colour, which renders its analogy with carotine closer, as carotine gives with the same reagent an indigo blue. The colouring matter is insoluble in water, and if injected into guinea-pigs and mice it occasions no disturbance of health.

The Condition of Chemical Instruction in the United States.—Prof. E. A. Schneider, of Chicago, gives in the *Chemiker Zeitung* the following severe condemnation of chemical instruction in the United States. He writes:—"The first question which the teacher hears from his pupils is, 'How soon can I complete my studies?' Just as in business it is thought meritorious to acquire wealth in the shortest possible time, honestly or dishonestly, a similar view prevails concerning the acquisition of a scientific capital. That such a way of thinking cannot produce eminent investigators, teachers, or technicists is manifest. It must be further remarked that the majority of American students are devoid of means. The rich do not allow their sons to study, or, if it happens, the education is confined to general culture, as offered by the various colleges. . . . In general it is only the 'poor devil' who devotes himself to a special study. How can a study requiring such an outlay of time and money as does chemistry prosper if the pupil has to devote part of the day to mechanical work to earn a livelihood, or to act as a waiter in the vacations, which is here a very frequent occurrence? The appointment of the professors lies exclusively in the power of the President of the University. This personage is in most cases a clergyman, often the favourite or the spiritual adviser of the millionaire benefactor or founder of the University, and is regarded by the Americans as a being endowed with omniscience." We have seen it asserted elsewhere that candidates for scientific chairs at American universities are sometimes interrogated by the President as to their views on some theological dogma.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Prevention of Frosting of Window Panes.—(Reply to J. Watson).—A solution of glycerin in water is thought to be useful in preventing moisture from forming on windows in cold weather, and so would be a remedy against the frosting. Equal parts of glycerin and water by measure might be tried, or nearly all glycerin. Repeat daily.—G. A. KEYWORTH, Hastings.

MEETINGS FOR THE WEEK.

TUESDAY, 26th.—Photographic, 8.
WEDNESDAY, 27th.—Society of Arts, 4. (Anniversary).
——— British Astronomical, 5.
THURSDAY, 28th.—Royal Society Club, 6.30. (Anniversary).

TO MANUFACTURING CHEMISTS.

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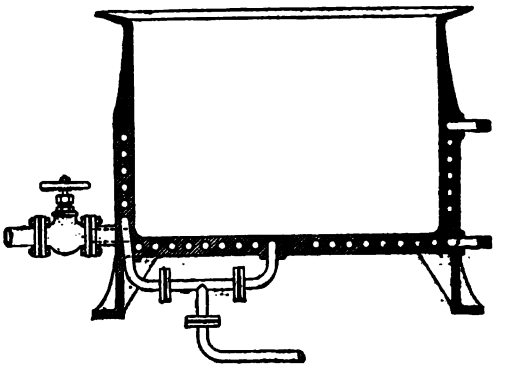

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says:—

P. 316. "An improved vessel for boiling oil, and suitable for many other kindred purposes, has been recently described by T. Frederking (CHEMICAL NEWS, London). A coil of stout piping is arranged in a casting mould, so that the molten metal forming the pan is cast round the coil, much as is done in the case of the water-tuyeres of a blast furnace. Steam at any pressure [or any other heating medium] being passed through the coil, the pan is heated up proportionately without any danger, the pressure bearing solely on the piping and not on the metal pan itself, whilst the well conducting metal walls allow the heat to pass readily. Temperatures up to 350° and 400° C. can be thus obtained."

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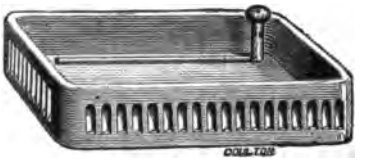

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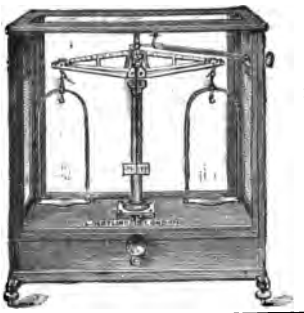

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12-inch Beam, with Agate Knife-edges, working on Agate Planes. Carries 100 grammes in each Pan, and turns with 0·1 milligramme. Beam-support descends. Polished Mahogany Glass Case, with counterpoise weights to front slide.

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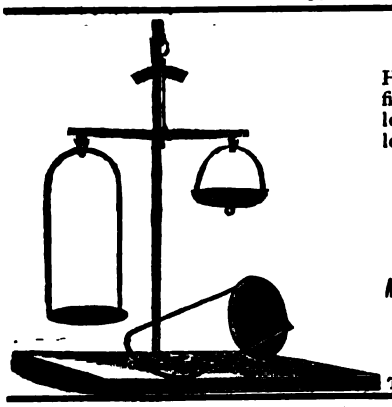

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Height, 27 inches; diameter of pans, 6¼ inches; length of beam, 14 inches fitted with two ordinary pans and one short pan for specific gravity. When loaded with 250 grammes in each pan it will turn with 0·1 gramme; when loaded with 100 grammes in each pan it will turn with 0·05 gramme.

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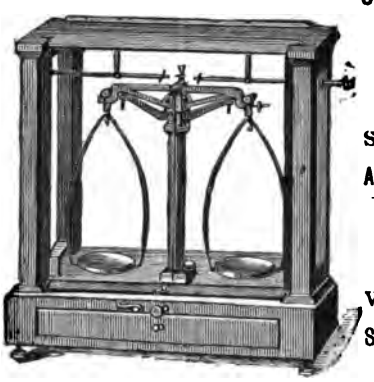

FIG. 3a.

SHORT BEAM BALANCE, No. 10a, Fig. 3a, to carry 100 grammes in each pan, and turn to 1-10th milligrm. Steel knife-edges, agate planes, two rider apparatus, and new improved arrangement for arrest of pans £8 15 0
Same with agate knife-edges £9 15 0

ANALYTICAL BALANCE, No. 7, to carry 50 grammes and turn to 1-5th milligramme. Steel knife-edges, agate planes, one rider apparatus, and new improved arrangement for arrest of pans £6 10 0
With agate knife-edges .. £7 10 0

STUDENT'S BALANCE, No. 69, to carry 30 grammes and turn to ½ milligramme £2 10 0

BALANCE No. 28, to carry 50 grammes and turn to ½ milligramme £2 16 8

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THE CHEMICAL NEWS.

Vol. LXIX., No. 1805.

RAILWAY AND CARRIAGE SPRING STEEL.

By SERGIUS KERN, M.E., St. Petersburg.

Our method gives steel which is more useful in comparison with the steel now ordinarily used for the manufacture of railway and carriage springs. Carriage springs means also material for all kinds of vehicles.

After hardening and tempering (the first operation at 900° C.), the new steel gives about 160 kilogrms. of tensile strength and 8 per cent of elongation. Therefore this steel has very good qualities for the construction of springs for railway purposes and common vehicles.

The chief and distinct parts of the new steel are the following:—

Limits.

Chromium	1·5 —2·0 per cent.
Combined carbon	0·35—0·45 ,,
Manganese	0·40—0·50 ,,

It is preferable to have for the manufacture of the new kind of steel rich ferrochromium (60—70 per cent of chromium) and ferromanganese (containing 80—85 per cent of manganese). The steel is manufactured either by the crucible process or in the Siemens-Martin furnace. In the first case the just mentioned alloys are placed with the charge of the crucibles; in the latter case the alloys are thrown into the furnace just before the casting.

The other elements, always present in all kinds of steel, must not exceed the following highest limits:—

A. *In Crucible Steel.*

Silicon	0·25 per cent.
Phosphorus	0·05 ,,
Sulphur	0·03 ,,

B. *In Siemens-Martin Steel.*

Silicon	0·05 per cent.
Phosphorus	0·06 ,,
Sulphur	0·05 ,,

We tested this method as early as in 1890, when we were in the service of the Pootiloff Iron and Steel Works, St. Petersburg. Several orders were executed and repeated with good results.

ANALYSIS OF SAMPLE OF ANCIENT SLAG.

By W. THOMASON.

The subjoined analysis is one performed upon a sample of slag derived from the Netherton district of Staffordshire. It has long been known as "Dud Dudley's" slag—indeed, from a period as remote as any authentic history of the district dates. It is of course certain that in this part of England "Dudley" did actually produce pig-iron by means of the blast furnace, his special improvement being the replacement of charcoal by "sea-coal" and "pit-coal" in the reduction. The substance is unquestionably a slag, as is demonstrated by the number of blow-holes contained in it and by its vitreous character.

Given its being a slag, it must be one of very great age, as is proved by its composition: iron = 38·13 per cent. It is hardly conceivable that this substance could have been a material of blast-furnace production, for the amount of lime in it is not more than could be accounted for by that usually present in the ores of the Staffordshire district.

The slag bears a marked resemblance to those produced by the old direct process for the manufacture of iron, in which process the siliceous matter and gangue are slagged off as a silicate of iron, $2FeO.SiO_2$. It would therefore appear that either the method of removing extraneous matter by means of lime was not at this time known, or that Dudley had, in addition to making pig-iron, also produced malleable iron by one of the older and better known direct processes.

Whatever mode of manufacture has been adopted, it is manifest that the materials have been caused to produce their own slags without the addition of any substance of basic character calculated to remove the siliceous matter with as little loss to the metal required as possible.

Analysis:

FeO	= 41·90 p.c.				
Fe_2O_3 ..	= 7·92 ,,				
MnO	= 0·20 ,,				
Al_2O_3 . ..	= 15·82 ,,				
CaO	= 2·24 ,,	Sulphur	= 0·024 p.c.		
MgO	= 1·73 ,,	Phosphorus ..	= 0·424 ,,		
K_2O	= 1·15 ,,				
Na_2O . ..	= 0·72 ,,				
SiO_2	= 28·15 ,,				
Total ..	= 99·83 ,,				

The mounds of this substance, which were at one time found in large numbers in this locality, have been gradually disappearing, being worked up by the modern iron works in the vicinity.

The Laboratory,
28, Chapel Street, Liverpool.

ON THE ORIGIN OF GOLD NUGGETS.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

(Continued from p. 298).

Expt. 34, *with Graphite, Ceylon.*—Decolourised several charges of solution. The gold plate was frosted (moiré métallique) on one side, and had increased 0·0001 grm. in fifty-nine days.

Expt. 35, *with Charcoal.*—Decolourised many successive two-ounce charges of gold solution, and the charcoal became thickly coated with dull brown gold; under microscope this was seen to be mammillated. The plate increased 0·00005 grm. only in fifty-nine days.

Expt. 36, *with Coal Powder.*—The gold plate was still bright when removed, on May 31st, 1893, *i.e.*, after thirty-five days, and had lost 0·0019 grm. On burning off the coal spongy brown gold was left mixed with the coal ash.

Expt. 37, *with White Sandstone, Sydney.*—The gold plate gradually acquired a frosted appearance and became stained of a dull brown colour. Under the microscope the frosting was seen to be due to the gold having crystallised in the same way that zinc crystallises on galvanised iron and tin in the moiré-metallique; the crystals on the gold plate were nearly all square or rectangular in outline and about 1 m.m. across. From April 26th to May 31st, 1893, the plate increased 0·0007 grm. in weight.

Expt. 38, *with Reddish coloured Sandstone, Sydney.*—Foil became very dull and acquired a rough incrustation of gold. The foil increased 0·0060 grm. in weight in fifty-nine days.

Expt. 39, *with Sand, from April 26th to June 1st.*—Although one charge of two ounces of the gold chloride was decolourised and another about half decolourised, the

* A Paper read before the Royal Society of New South Wales, September 6, 1893.

No.	Name of substance placed with the gold plate.	Diff. in weight in grms.	Length of expt. Days.
10.	Molybdenite	+0·0038	59
11.	Mispickel	+0·0006	59
12.	,, ...	+0·0260	59
13.	,, ...	+0·0089	9
14.	Recent iron pyrites, Loffley's	none	59
15.	Cubical iron pyrites	+0·0028	59
16.	Iron pyrites, Joshua's Spa ..	+0·0060	59
17.	Iron pyrites	+0·0708	9
18.	Iron pyrites	+0·0633	9
19.	Rhombic iron pyrites, or marcasite	+0·0328	9
20.	Brown hæmatite	+0·0003	59
21.	Limonite	+0·00025	59
22.	Rust	+0·0011	59
23.	Copper pyrites..	+0·0059	59
24.	Copper pyrites..	+0·0185	59
25.	Copper pyrites, Walleroo, S.A.	+0·0666	9
26.	Redruthite (copper subsulph.)	+0·0836	9
27.	Silver sulphide (argentite) ..	+0·0083	155
28.	Fused artificial silver sulphide	+0·0082	9
29.	Galena	+0·0049	59
30.	Galena, Broken Hill, N.S.W.	+0·0281	9
31.	Zinc blende	none	59
32.	Zinc blende	+0·0086	9
33.	Graphitic casing	none	
34.	Graphite, Ceylon	+0·0001	59
35.	Charcoal	+0·00005	59
36.	Coal powder	−0·0019	35
37.	White sandstone, Pyrmont ..	+0·0007	35
38.	Sandstone, reddish	+0·0060	59
39.	Sand	none	36
40.	Gravel, Bingera Diamond Fields, N.S.W.	−0·0008	59
41.	Wash-dirt, Inverell, N.S.W.	+0·0003	9
42.	Granite, Hartley, N.S.W. ..	+0·0006	59
43.	Granite, Hartley, N.S.W. ..	+0·0002	59
44.	Quartz, white	+0·0002	59
45.	Clay, University Paddock ..	+0·0019	59
46.	Statuary marble	+0·0002	59
47.	Apatite, Canada	none	200
48.	Serpentine	+0·0001	59
49.	Plate glass	+0·00005	59

plate underwent no change in weight. The solution was doubtless reduced by organic matter present in the sand.

Expt. 40, *with Gravel, from Bingera Diamond Mines.*—Solution not decolourised, but the plate lost 0·0008 grm. in fifty-nine days.

Expt. 41, *with Wash Dirt, Inverell, N.S.W.*—Minute flakes of bright gold were found intermingled with the clay from this dirt. Foil increased 0·0003 grm. Decolourised two charges, *i. e.*, four ounces of the solution.

Expt. 42, *with Granite, Hartley, N.S.W.*—Foil became dull and stained on one side, and had increased 0·0006 grm. in weight in fifty-nine days.

Expt. 43, *with Granite, Hartley, N.S.W.*—The powder of this granite turned brown like a pale clay; the foil became dull, much stained, and increased 0·0002 grm. in weight in fifty-nine days.

Expt. 44, *with White Quartz.* — Decolourised two ounces of the solution, and a second two ounces partly; increase in gold plate, 0·0002 grm. in fifty-nine days.

Expt. 45, *with Clay, University Paddock.*—Decolourised several charges. Foil became dull, and increased 0·0019 grm. in weight in fifty-nine days.

Expt. 46, *with Statuary Marble.*—This decolourised two ounces of the solution before the addition of the gold plate and several successive charges after; the plate darkened in colour and increased 0·0002 grm. On dissolving the marble in hydrochloric acid a residue of brown mammillated gold was left.

Expt. 47, *with Apatite, Canada.*—As the solution was not decolourised after two hundred days, the gold foil was not re-weighed.

Expt. 48, *with Serpentine, containing a little Magnetite.*—Decolourised four ounces of gold solution, but the plate only showed an increase of 0·0001 grm. in fifty-nine days.

Expt. 49, *with Plate Glass, in Powder.*—Before the plate of gold was added the glass reduced two ounces of the solution; and on June 1st it had reduced the second two ounces. The plate increased 0·00005 grm. in weight in fifty-nine days.

The Table shows that in forty experiments there was a loss of gold from the nucleus in two cases, in five others there was no change, but in thirty-three there was an increase in weight, this increase varying from 0·00005 grm. to 0·0836 grm. The heavier deposits could be separated as a continuous film by bending the gold plate backwards and forwards a few times.

The foregoing experiments show that gold is deposited from solution upon a nucleus of gold in contact not only with metalliferous sulphides and arsenides, which form strong galvanic couples, but also with such substances as iron oxides, charcoal, graphite, sandstone, granite, quartz, clay, and marble, which form but weak galvanic couples with the gold plate, and, as we might expect, the deposition goes on more slowly in the latter cases. In Daintree's experiment the glass of the bottle may have formed a couple with the gold fragment.

(To be continued).

DETECTION OF SMALL QUANTITIES OF NITROUS ACID.

By P. GRIESS.

The author proposes to acidify the liquid in question with sulphuric acid, to add a little solution of sulphanilic acid, and then a few drops of a solution of naphthylamine decolourised with animal charcoal, when the presence of nitrous acid is shown by a red colour.

This reaction, according to G. Lunge, is open to the objection that the solution of α-naphthylamine, even if a perfectly white salt is used, darkens after a short time, and the reaction loses sensitiveness. In very dilute solutions, *e.g.*, 1 : 1000 millions, the reaction takes place so slowly that it may be doubtful whether the nitrous acid may not have been derived from the air. The time may be abridged by the application of heat, but even then it may require from fifteen to twenty minutes.

Ilosway states that the use of acetic acid instead of sulphuric or hydrochloric acid expedites the reaction and renders the colour much more sensitive. He alleges that the darkening of the naphthylamine may be prevented by boiling solid naphthylamine in water and using only the aqueous solution decanted, whilst still hot, from the residue.

For preparing the solutions, Ilosway dissolves 0·5 grm. sulphanilic acid in 150 c.c. dilute acetic acid.

He boils 0·1 grm. solid naphthylamine with 20 c.c. water, decants off the colourless solution from the violet-blue residue, and adds 150 c.c. dilute acetic acid.

The liquid to be tested for nitrous acid (about 20 c.c.) is mixed with a few c.c. of the solution of sulphanilic acid, and the solution of naphthylamine is then added. If nitrous acid is present to the extent of 1 : 1000 millions, the red colour appears in a minute. If the quantity of nitrous acid is greater, about 1 : 1000, we obtain a yellow solution, unless a more concentrated solution of naphthylamine is used.

Lunge confirms the statements of Ilosway, and has still further improved the procedure. The reaction for nitrous acid is quite as intense if Ilosway's solutions of sulphanilic acid and naphthylamine are at once mixed together and kept in stock in a well-stoppered bottle. Exclusion

of air is essential. The action of light is unimportant. If both reagents are mixed together, the liquid is reddened in the bottle by the nitrous acid in the air, it may then be again rendered fit for use by shaking up with zinc powder and filtering.—*Zeitschr. f. Anal. Chemie.*

HEINRICH HERTZ.*

By HERMANN EBERT.

The two last decennial periods have robbed us of not a few distinguished men. But for the most part they had already worthily played their part, and their loss was to be expected in the ordinary course of nature. Different was the case with Heinrich Rudolf Hertz.

The fruitful researches with which he had at once astonished and delighted his contemporaries had been accomplished in the brief span of thirteen years. Hence his death at the early—premature as it seems to us—age of thirty-seven, forces us to reflect how much more he might have effected had he been favoured with a longer life.

He was born February 22, 1857, at Hamburg, entered the "Johanneum" gymnasium of his native city at Easter, 1874, which he left in 1875, with testimony of maturity ("Maturitäts Zeugniss"), which denotes that the recipient is qualified to enter upon his university career. In addition to his studies, he acquired a practical training at the lathe and the planing bench, and succeeded in constructing a spectroscope.

On leaving the gymnasium, he devoted himself to the study of architecture. During the year 1875—76 he entered the municipal building department at Frankfurt. In the summer term of 1876 he joined the Technical High School at Dresden. His studies were then interrupted by a one-year's military service. In the autumn of 1877 he went to Munich, where he experienced a change in his views, and from being an engineer he became a *savant*. He devoted himself especially to mathematics and physics. In 1878 he removed to the University of Berlin, and entered the laboratory of Prof. von Helmholtz. In 1880 he took his Ph.D., and became Helmholtz's assistant at the Physical Institute. In 1885 he was nominated Professor of Physics at the Technical High School of Karlsruhe. In the following year he married Elizabeth Doll, the daughter of the Professor of Geodetics at the same College. In 1889 he had the singular honour of being called to Bonn as the successor of Clausius. In the middle of 1882 he was attacked by chronic blood poisoning, and after intense suffering he died on January 1st of the present year.

Passing over his other researches, we see that his chief merit lay in his wonderful electrical discoveries. As the author before us says:—"He delivered us from the theories of *actio in distans*, showing that electric and magnetic effects are diffused with finite speed through space from particle to particle. This is a result of high general philosophic significance. The dogma hitherto consecrated by Science, but unwillingly tolerated by reason, that anything can act where it is not, has lost its value for electric and magnetic effects."

The identity of the kind of energy of two mighty natural agencies is irrefutably demonstrated. The sphere of optics has been enormously extended. To the ultra-violet, the visible, and the infra-red rays, with their wave-lengths, measuring only the thousandth of a millimetre, there have been added rays of many metres of wave-length. The scale of colours is infinitely enlarged, although the rods of our sight-organ do not react to the new vibrations.

Hertz has brought us nearer the solution of the burning question: "What is electricity?" He has seen that there is no electricity in the sense of the fluid of the old theories. The phenomena to be explained are *conditions* in the ether which pervades all things.

Glancing at what Hertz has effected in so short a time, we can merely think of what he might have realised. In any case we must place his name high among the ranks of those creative minds to whom we are indebted for our Science.

* A Memorial Discourse delivered in the General Session of the Physiko-Medical Society of Erlangen, March 7, 1894, and reprinted from its *Transactions*.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 7th, 1894.

Dr. ARMSTRONG, President, in the Chair.

Certificates were read for the first time in favour of Messrs. Henry Spencer Blacmore, 206, South 9th Avenue, Mount Vernon, New York; Joseph F. Chambers, Grammar School, Dursley, Gloucester; William Dixon, 102, Spring Street, Bury, Lancashire; Frederick Dunn, 83, Packington Street, Kew, Melbourne; Martin Stanyer Higgs, Clarence House, Gloucester; James Knight, 121, Kenmure Street, Pollokshields, Glasgow; Charles Stirling Saunders, 163, Victoria Street, Westminster; Cuthbert Vaux, 11, Thornhill Park, Sunderland; John Cundell Wood, 3, Bedford Terrace, Sunderland.

The following were duly elected Fellows of the Society:—George Dixon, George Donald, Nicholas Eumorfopoulos, Robert John Flintoff, Bhikaji Edalji Ghasvala, Arthur Hadley, Sydney Walters Harris, J. H. Hitchens, Wilmot Holt (jun.), Arthur Peach Hope, James McLeod, G. S. Newth, Alfred Nixon, G. L. Parker, E. Brooke Pike, Herbert Harold Robjohns, John F. Rolfe, George Ryce, Herbert Stephen Shorthouse, Professor Edward B. Shuttleworth, Ernest Alfred Smith, John George Spenzer, M.D., Ph.D., Robert W. Steel, Herbert John Taylor, Edward Cumming Thompson, George Dupré Thudichum, Charles H. H. Walker, Arthur Swainson Waterfield, Robert Wright.

Of the following papers those marked * were read:—

*22. "*The Crystallography of the Normal Sulphates of Potassium, Rubidium, and Cæsium.*" By A. E. TUTTON, Assoc. R.C.S.

The author has made a detailed study of the goniometrical and physical characters of the crystals of these three salts, in order primarily to ascertain whether they exhibit any connection with the atomic weight of the metals contained. A very large number of goniometrical measurements were made upon particularly perfect crystals of the pure salts, and the physical measurements were carried out upon a similar scale. The results of the optical investigation have been merely enhanced in accuracy, and the observations themselves greatly facilitated, by the use of the instrument for grinding section-plates and prisms and the apparatus for illuminating the whole field of an optical instrument with spectrum monochromatic light of any desired wave-lengths, recently described by the author (*Proc. Roy. Soc.*, lv., 108 and 111). The main results of the investigation are the following:—

1. The normal sulphates of potassium, rubidium, and cæsium exhibit a graduated order of solubility corresponding to the order of the atomic weights of the three metals. Potassium sulphate is very sparingly soluble, cæsium sulphate is extremely soluble, and rubidium sulphate is soluble to an intermediate extent in water.

2. The habits assumed by the strictly isomorphous rhombic crystals of the three salts approach each other very closely, but the predominating relative amounts of development of the primary faces indicate a progression in the order of the atomic weights of the contained metals.

3. The magnitudes of the whole of the angles of the rubidium salt lie between those of the analogous angles upon the potassium and cæsium salts. The angular differences are much smaller than those exhibited by the monoclinic double sulphates previously investigated, indicating that such differences are smaller the higher the symmetry.

4. The axial ratios for rubidium sulphate are intermediate between those for potassium and cæsium sulphates, the ratio $a:b$ diminishes, but only very slightly, upon replacing potassium by rubidium, or the latter by cæsium, while the ratio $c:b$ increases materially. The conclusions in this and the preceding paragraph are independent of the temperature.

5. The relative density, which has been determined with the greatest care upon a large number of samples of the pure salts, and molecular volume of rubidium sulphate, are intermediate between the values of these constants for the potassium and cæsium salts. A greater increase of volume accompanies the replacement of rubidium by cæsium than is observed when rubidium replaces potassium, but the difference is not so large as that derived from Pettesson's determinations of the densities, he having worked with much smaller quantities of the salts, and in the case of cæsium sulphate with impure material.

6. The coefficients of cubical expansion, derived from determinations of density at higher temperature, are almost identical, the differences being about the limits of experimental error. Determinations of the linear thermal expansion indicate that the greatest amount of expansion occurs in the direction of the vertical axis c, the expansion along the other two axes being more nearly equal.

7. The distance-ratios (topic axes of Muthmann) of the crystal-elements (physical molecules), obtained by combining the axial ratios with the molecular volumes, indicate that the replacement of potassium by rubidium and rubidium by cæsium is accompanied by an increase in the separation of the crystal-elements along each of the axial directions, and this increase is relatively much greater when cæsium replaces rubidium than when the latter replaces potassium. The amount of increase is greatest along the b axis and least along the a axis, but if the amount of increase is considered proportionally to the lengths of the axes, the change along the c axis is greater than in proportion to the length of that axis, while the changes along the a and b axes are almost in exact proportion to their lengths.

8. The directions of cleavage, the positions of the planes in which the elementary parallelograms occupy least area, and the nature of the forms exhibited by the crystals, agree in indicating that the elementary parallelopiped of the series is a rectangular rhombic prism. The order of change in the distance-ratios can be fully accounted for upon the supposition that the crystal-element of the series is composed of four chemical molecules, symmetrically arranged with respect to the three planes of rhombic symmetry.

9. An increase of refractive power accompanies an increase in the atomic weight of the contained metal, and the increase becomes relatively greater as the atomic weight rises. Hence the intermediate refractive indices and optical elasticity constants of rubidium sulphate are nearer to the potassium than to the cæsium salt. The ellipsoidal wave-surface, of rays emanating from a common central point, for rubidium sulphate lies between the wave-surfaces of potassium and cæsium sulphates respectively, and nearer to the outer enveloping wave-surface of the potassium salt than to the inner one of cæsium sulphate.

10. The amount of diminution of optical elasticity on passing from one salt to another is almost identical in the axial directions a and b, but is much less along the axis c. This causes a reversal in the order of double refraction, the potassium salt being endowed with positive and the cæsium salt with negative double refraction. The intermediate value which the elasticity along the axis c assumes in the rubidium salt happens to fall so close to the value along the b axis, and between that value and the already closely lying value along the a axis, that crystals of rubidium sulphate exhibit extraordinarily low double refraction, and the optic axial angle exhibits very large dispersion for different wave-lengths.

11. A regular decrease in refractive power and corresponding increase of optical elasticity is observed as the temperature is raised. This change is likewise greatest along the c axis, and the lesser changes along the a and b axes are approximately equal. The relations, however, are the same as at the ordinary temperature, rubidium maintaining its intermediate position. The greater change along the c axes causes a remarkable alteration in the optic axial angle of rubidium sulphate. A few degrees of rise of temperature are sufficient to bring the value along the c axis identical with that along the b axis, and afterwards to overstep that value. Hence, before warming a section-plate perpendicular to the first median line, the hyperbolic brushes indicating the loci of the optic axis are observed to approach the centre, and, for the different wave-lengths in succession, owing to the large dispersion, to unite and produce an uniaxial figure. This occurs at about 40° for red light and 65° for violet light. Further heating causes the brushes to separate in the plane at right angles to that which previously contained them.

12. The molecular refraction and dispersion, whether calculated by the formula of Lorentz or Gladstone and Dale, increase with the atomic weight of the contained metal, rubidium sulphate being also intermediate in this respect. The increase becomes greater as the atomic weight rises, and proceeds at a slower rate along the c axis than along the a and b axes, along which latter directions the changes are almost identical. These relationships are independent of the temperature.

13. With regard to every property, whether morphological or physical, it has been found that rubidium sulphate stands intermediate between the potassium and cæsium salt. The replacement of rubidium by cæsium is generally accompanied by a greater modification of the crystallographical characters, than when potassium is replaced by rubidium, the heavier atom exerting an influence greater than in mere simple proportion to the increase in atomic weight. The comparative results for the different properties are all in line with each other, the relations of the amounts of change along the crystallographic axes being similar with regard to all. Moreover, the progression, according to the atomic weight of the contained metal, is perceptible with regard to the minutest details of the physical phenomena presented by the crystals, and is entirely independent of the temperature. The author therefore finally concludes that—

"The whole of the crystallographical properties of the strictly isomorphous, rhombic, normal sulphates of potassium, rubidium, and cæsium, are functions of the atomic weight of the metal which they contain."

Discussion.

Mr. Miers was of opinion that Mr. Tutton had established the relations between these sulphates with absolute certainty, and had determined their characters with greater accuracy than had ever yet been done for any crystallised series. He believed, however, that all conclusions drawn from the crystal form alone regarding the relative positions of the atoms in the crystal molecule must at present be regarded as nothing more than speculations. Additive relations, as in the Humite group of minerals, where successive additions of the radicle Mg_2SiO_4 produce *equal* changes in the length of one crystallographic axis alone are extremely suggestive; but the method of Muthmann and Mr. Tutton requires us to assume the exact form of the elementary parallelopiped, of which we have no knowledge. If the symmetry of the molecule is supposed to be the same as that of the crys-

tal, we encounter a further grave difficulty in the case of those isomorphous compounds which have nearly the same form and yet belong to different systems; for the replacement of one radicle by another in a symmetrical group should not disturb the symmetry if the arrangement remains the same. Such speculations have yet to be tested by physical characters.

*23. "*Observations on the Nature of Phosphorescence.*" By Herbert Jackson.

This paper deals, first, with the readiness with which the phenomena of phosphorescence may be studied by using a mechanical pump capable of very rapidly giving high vacua (Fleuss's pump).

The author considers that in many cases the phosphorescence cannot be ascribed to impurities, but that a presumably pure substance yields in several instances phosphorescence of different colours.

The main portion of the paper is occupied with an attempt to show that the phenomena of fluorescence, phosphorescence in air on exposure to light, and phosphorescence of substance in a vacuum under the influence of the electric discharge, are of the same nature, viz., a response on the part of the substances to the operation of radiant energy propagated after the manner of light in undulations of short length.

These undulations proceed from the electrode, and to them the gas in the tube responds, giving rise to the visible light in the gas.

To this light some phosphorescent bodies respond; but others require to be affected by the very short undulations to which air is opaque. Such substances therefore only phosphoresce in high vacua.

These conclusions are based on experiments made with a "jar spark" in air acting upon phosphorescent substances placed in the appropriate foci of a quartz lens; on the study of the behaviour of such substances outside a vacuum tube provided with a quartz window, and also on their behaviour inside the vacuum tube.

The results of a very large number of experiments seem to indicate a close connection between the phenomena of phosphorescence in air, and in a vacuum, broken only when the opacity of quartz to some undulations and of air to others interferes.

Discussion.

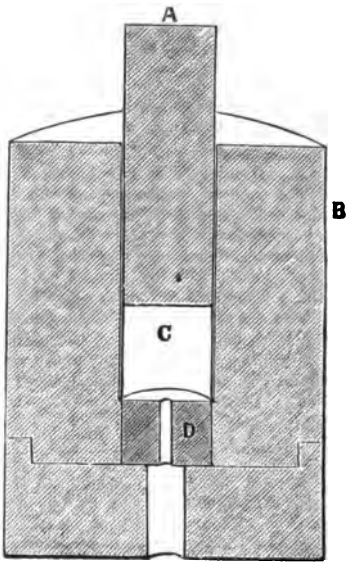
Professor Dewar stated that he had recently made a series of experiments on photographic action and phosphorescence at temperatures between −180° and −200° C. The majority of substances under such conditions show more or less phosphorescence, and some, like cotton-wool, paraffin, the alcohols, ketones, acids, &c., are remarkably brilliant. Substances that at ordinary temperatures are said only to be fluorescent, become phosphorescent owing to the combined effect of greater and differently distributed absorption and the lengthening of the period of dissipation when light rays are emitted.

Mr. Jackson remarked that he had found the phosphorescence of some substances could only be observed after they had been cooled in solid carbon dioxide dissolved in ether, while in the case of other substances they required first to be raised above the ordinary temperature.

The President pointed out that the great simplification in the method of producing phosphorescence introduced to their notice by the author would much facilitate the study of the spectra of substances phosphorescing in high vacua—a class of spectra which, to judge from Mr. Crookes's researches, were especially valuable in differentiating the rare earths.

*24. "*Note on the Viscosity of Solids.*" By James Dewar, F.R.S.

The experiments of Tresca on the flow of metals are well known, as are also the observations of Spring on the cohesion of powdered substances under pressure. It appears that few, if any, systematic experiments have been made on the viscous flow of solid salts and organic compounds. The following apparatus was used in the experiments:—



B is a strong steel block with a tight-fitting piston of the same metal; the narrow tube through which the substance was squeezed is represented by D, and C is the space filled with the substance. The diameter of the narrow steel tube D was $\frac{1}{16}$ inch, and the length $\frac{1}{4}$ inch. In the following experiments the maximum theoretical pressure was 60 tons on the square inch; this being determined from the relation between the diameters of the piston A and that of the hydraulic press used in the experiments, together with the pressure observed in the latter. The easily flowing bodies generally flow above 30 to 40 tons pressure. The substances experimented upon may be divided into two groups: those forming a wire under the conditions, and those which hardly show any trace of viscosity. It is to be understood that each experiment did not last longer than from five to ten minutes on the average. The ordinary hydrated salts are distinguished by the addition of "aq."

Bodies which flow into wire:—Sodium sulphate, aq, sodium carbonate, aq, sodium thiosulphate, aq, magnesium chloride, aq, ferrous sulphate, aq, ammonium chloride, potassium chloride, bromide, iodide, cyanide, nitrates of ammonium, potassium, and silver, strontium chloride, aq, aluminium sulphate, aq, caustic soda, oxalic acid, aq, sodium acetate, calcium chloride (slow), acetamide (slow), lead acetate (slow), benzoic acid (slow), graphite (easy, brittle wire), iodine (easy, long continuous wires), urea (easy), anthraquinone (very slow, brittle).

Bodies which do not flow into wire:—Sodium phosphate, aq, borax, aq, alums, sodium nitrate, chloride of sodium, lithium, zinc, mercury, sulphide of manganese, aq, ammonium sulphate, sodium oxalate, ferrous oxalate, rochelle salt, arsenious oxide, potassium ferrocyanide, sodium acetate, ammonium acetate, aq, nitrates of barium, strontium, caustic potash, dry carbonate and sulphate of sodium, dry sulphide of aluminium, sugar, starch, naphthalene.

Many of these substances explode through the narrow orifice in sudden bursts rather than form any wire, and such a sudden shock has on two occasions caused the fracture of the strong steel cylinder. These preliminary results are sufficient to show that the explanation of the cause of the flow of solid matter in the class of bodies under consideration will require prolonged investigation. No doubt many of the substances which do not flow (or only do so with extreme slowness) at 60 tons on the

square inch, may do so at much higher pressures. It would appear, however, that in each case the substance has a limiting pressure which must be reached before a reasonable rate of flow is attained, and this value is probably a constant. The rate of flow of fused sulphocyanide of ammonia at 60 tons is about one inch a minute.

25. "*Boiling-points of Homologous Compounds.*" Part II. By JAMES WALKER.

The author has now applied his formula $T = aM^b$ (*Trans.*, 1894, 193) to the normal fatty acids, their ethereal salts, the normal hydrocarbons, the normal alkyl chlorides, and other series of compounds, and finds that on the whole it gives satisfactory results. The only pronounced exceptions are the series of the alkyl bromides and alkyl iodides.

The formula is valid for the boiling-points at pressures other than the atmospheric pressure, the constant a alone varying from pressure to pressure. A deduction from the constancy of b in such cases is that in any homologous series the ratio of the absolute boiling-points at two different pressures is the same for all members of the series. This deduction is confirmed by the experimental data.

26. "*The Action of Methyl Iodide on Hydroxylamine.*" By WYNDHAM R. DUNSTAN, F.R.S., and ERNEST GOULDING.

In the current number of the *Recueil des Travaux Chimiques des Pays Bas*, M. Lobry de Bruyn gives an account of experiments he has made on the action of methyl iodide on hydroxylamine. He states that when the iodide is mixed either with a solution of free hydroxylamine or with an alkaline solution of hydroxylamine hydrochloride, β-methyl hydroxylamine hydriodide, $CH_3NH{\cdot}OH,HI$, is readily produced, and separates in crystals from the liquid, so that by this means the compounds of β-methyl hydroxylamine, which have hitherto been troublesome to prepare, are readily obtained in a pure state; and, similarly, it would appear that the process is applicable to the preparation of other β-alkyl hydroxylamines.

The authors have for some time been engaged in similar experiments also, in the hope of discovering a simple mode of preparing β-alkyl hydroxylamines, but the results they have obtained do not correspond with those of M. de Bruyn. Working with a solution of free hydroxylamine, distilled according to De Bruyn's method, interaction with methyl iodide occurs immediately with evolution of heat. After the action is over a white crystalline salt separates from the mixture, and a further quantity may be obtained by adding ether to the solution. This substance consists almost entirely of a *trimethyl hydroxylamine hydriodide*. The authors have not succeeded in obtaining any considerable quantity of the monomethyl derivative described by De Bruyn. The salt of the trimethyl base is easily purified by crystallising it from a mixture of methyl alcohol and ether. It melts with decomposition near 127°. The *hydrochloride* (m. p. 200°) and the *sulphate* are stable crystalline salts, which may be crystallised from water without decomposition. By the action of baryta water on the sulphate, or of silver oxide on the hydriodide, the free trimethyl hydroxylamine was obtained. It crystallises readily and is remarkable for its stability; the aqueous solution does not reduce Fehling's solution, and may be boiled without undergoing any appreciable change. The properties and reactions of this interesting compound are being fully investigated.

The authors' experience is that the action of alkyl iodides on hydroxylamine does not constitute a satisfactory process of preparing β-mono-alkyl derivatives of hydroxylamine. They hope shortly to be able to give a more detailed account of their work, which is still in progress.

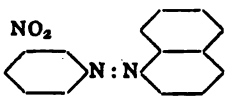
27. "*The Reduction Products of Nitro-compounds.*" By WYNDHAM R. DUNSTAN, F.R.S., and T. S. DYMOND.

The authors have conducted a number of experiments on the reduction of aliphatic nitro-compounds with various weak reducing agents. They have obtained evidence of the formation under certain conditions of the corresponding *aldoximes* or *ketoximes*, nitroethane furnishing acetaldoxime, nitropropane propionaldoxime, secondary nitropropane, acetoxime, &c. In addition, substituted hydroxylamines are produced, as first observed by Victor Meyer and recently by Bamberger, as well as the corresponding amines. The aldoxime or ketoxime would appear to be an early, if, indeed, not the first, product of the reduction of the nitro-paraffins.

During the past year the authors have been unavoidably prevented from continuing this enquiry, but one of them has now resumed it. It is hoped that a method of reduction may be found which will give a large yield of the oxime; hitherto the amount produced has been very small, and therefore the oxime is difficult to isolate and characterise. An attempt is being made to ascertain whether the formation of the aldoximes or ketoximes is to be regarded as an intermediate stage in the reduction of the nitro-compound to the substituted hydroxylamine as represented by the diagram—

$$CH_3CHN{\cdot}OH \rightarrow CH_3CH{:}NOH \rightarrow CH_3CH_2NHOH$$
$$\quad\quad\quad

composition is completed by boiling as long as nitrogen is evolved, the cold solution filtered to remove the resinous impurity, and the alcohol partly evaporated off. On diluting the final alcoholic liquor with water, the nitroazo-compound separates out after some hours in the form of fine red needles. The substance was purified by crystallisation from dilute alcohol with animal charcoal, and finally from benzene. It was thus obtained in the form of stumpy prisms of a deep red colour, melting at 127—128°. Analysis showed that the NH_2 group had been replaced by hydrogen, and the formula of the compound is, therefore,—



Calculated for above formula 15·16 per cent N; found 15·03 per cent. Metanitrobenzeneazo-α-naphthalene is readily soluble in alcohol and benzene, its solutions being orange.

It dissolves in strong sulphuric acid with a violet colour, becoming redder on dilution with water.

Several attempts to replace the amido-group by hydrogen in metanitrobenzeneazo-β-naphthylamine (*Trans.*, 1884, 116) resulted in the formation of metanitrobenzeneazo-β-naphthol (*Trans.*, 1885, 668).

Experiments were in the next place undertaken with a view to ascertain whether a more satisfactory yield could be obtained from a simpler nitroamidoazo-compound, viz., metanitroamidoazobenzene (*Trans.*, 1884, 112). As this compound, which was described by one of us ten years ago, was not isolated in a state of purity at the time of its discovery, a further study of its mode of formation and properties was undertaken. Our experiment prove that the most advantageous method of preparing this compound is to combine diazotised metanitraniline with aniline in the presence of sodium acetate so as to form in the first place the mixed diazoamide,—

$$(m)NO_2\cdot C_6H_4\cdot N_3H\cdot C_6H_5,$$

in the usual way. This compound is collected, washed well with water, and then transferred to a flask or beaker and allowed to stand for two or three days suspended in dilute hydrochloric acid. The strength of the acid may be increased from day to day, and finally the contents of the vessel must be kept at 80—90° in a water-bath till no more nitrogen is evolved. The transformation of the diazoamide takes place very well by this method, and by this method only. The usual process of transforming, viz., warming with aniline and aniline hydrochloride, gives a mixture of metanitraniline and amidoazobenzene,

$$NO_2\cdot C_6H_4\cdot N_3H\cdot C_6H_5 + C_6H_5\cdot NH_2 = NO_2\cdot C_6H_4\cdot NH_2 + C_6H_5\cdot N_3H\cdot C_6H_5.$$

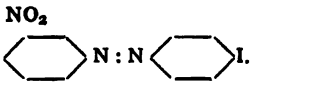
The yield of crude nitroamidoazobenzene obtained by the hydrochloric acid method is not very great, averaging in various preparations about 30 per cent of the metanitraniline employed. A large quantity of metanitraniline is found in the acid filtrate, and can be recovered by precipitation with alkali, and purified by crystallisation from hot water.

In order to purify the nitroamidoazobenzene, the crude product is dissolved in hot alcohol with the addition of strong hydrochloric acid, filtered when cold to remove tarry impurity, and the solution made alkaline with ammonia, and diluted with water. The base separates out as an orange crystalline powder, and the process of purification must, if necessary, be repeated. The substance is finally crystallised from dilute alcohol or toluene. To the properties of the compound as described in 1884 we have but little to add. When pure it melts without decomposition at 212—213°. The nitro-group practically destroys the basic character of the compound, which is quite insoluble in dilute aqueous acids, and dissolves only with difficulty in alcohol and hydrochloric acid. In order to further characterise it, the acetyl derivative was prepared by boiling the substance for a short time with glacial acetic acid and acetic anhydride. The product after crystallisation from alcohol formed orange scales melting at 166—167°. Calculated for—

$$NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NH\cdot C_2H_3O,$$

19·71 per cent N. Found, 19·91 per cent N.

Metanitroparaiodoazobenzene was also prepared by diazotising the base dissolved in strong sulphuric acid, diluted with about an equal volume of water, and mixing with a solution of potassium iodide. After crystallisation from alcohol, the compound consists of ochreous needles, melting at 123—124°. Calculated, 11·89 per cent N; 35·97 per cent I. Found, 12·11 per cent N; 36·15 per cent I. The constitution is doubtless



An azimide was prepared by diazotising the compound in sulphuric acid solution with sodium nitrite, adding bromine and decomposing the diazoperbromide with ammonia in the usual way. The perbromide separates as a red oil, which solidifies to a crystalline cake on standing. The azimide, after repeated crystallisation from dilute alcohol with animal charcoal, consists of white needles, melting at 80°.

Calculated for $(m)NO_2\cdot C_6H_4\cdot N_2C_6H_4\cdot N_3(p)$, 31·34 per cent N.

Found, 31·11 per cent.

By diazotising the nitroamidoazo-compound in the presence of sulphuric acid, and boiling the diazosulphate with water, a phenolic product was obtained, having all the properties of metanitrobenzeneazophenol.

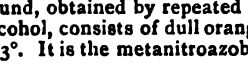
We did not have enough of the substance to obtain a pure specimen for analysis, but some of the compound obtained by combining diazotised metanitraniline with phenol in alkaline solution was prepared for comparison, and we are satisfied as to their identity. The product obtained by pouring a solution of metanitrodiazobenzene chloride into an alkaline solution of phenol always contains a small quantity of a by-product insoluble in cold dilute caustic soda, and consisting, probably, of the disazo compound, $[(m)NO_2\cdot C_6H_4\cdot N_2]_2\cdot C_6H_3\cdot OH$.

Metanitrobenzeneazophenel, when purified by crystallisation from toluene, forms deep orange-red nodular crystals, melting at 159°. Noelting, who first prepared this compound, gives the melting-point as 146—147° (*Ber.*, 1887, 2998), a discrepancy for which we are unable to account. Analysis proved our preparation to be quite pure. Calculated, 17·28 per cent nitrogen; found, 17·31 per cent.

The NH_2-group was eliminated from the nitroamidobenzene in the following manner:—4 grms. were dissolved in 200 c.c. absolute alcohol, a few drops of strong sulphuric acid added to the cold solution, and the calculated quantity of sodium nitrite, dissolved in a little water, poured in.

The mixture is then boiled for an hour, the alcohol evaporated off, and the product thrown out by adding water.

The yield is by no means good, as much resin is formed. The pure compound, obtained by repeated crystallisation from absolute alcohol, consists of dull orange-red needles, melting at 82—83°. It is the metanitroazobenzene sought for—



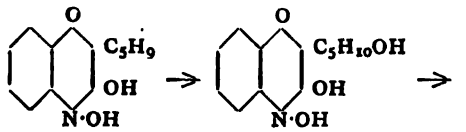
Calculated, 18·50 per cent nitrogen; found, 18·38 and 18·39 per cent.

The nitro-group could not be reduced without simul-

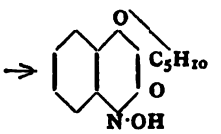
taneous separation of the azo-group, so that the desired metamidoazobenzene could not be prepared from this compound.

29. "*Conversion of Ortho- into Para-, and of Para- into Ortho-Quinone Derivatives.* III. *The Hydroximes of the Lapachol Group.*" By SAMUEL C. HOOKER and ELWOOD WILSON.

The authors have found that by the action of mineral acids upon the hydroximes of lapachol and hydroxyhydrolapachol the same compound is formed in both cases, and that this is identical with the hydroxime obtained by Paterno and Minnuric (*Gazzetta*, xix., 613) by treating β-lapachone with hydroxylamine hydrochloride. From these facts they deduce the following formulæ for the compounds studied.

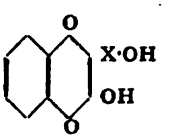


Lapachol hydroxime. Hydroxyhydrolapachol hydroxime.



β-Lapachone hydroxime.

Evidence is thus furnished that the substitution of the diad group=N·OH for the quinonic oxygen, does not modify the tendency which, as has been previously shown by one of the authors, frequently exists for compounds of the type—



to form anhydrides derived from β-naphthaquinone.

The hydroxime of α-lapachone is also described, and it is shown that it can be converted by concentrated sulphuric acid into β-lapachone-hydroxime, a change involving the conversion of the para- into the ortho-quinone group.

30. "*The Behaviour of Alloys in a Voltaic Circuit.* By A. P. LAURIE.

In former papers on this subject I have shown that there is reason to believe, owing to the remarkable discontinuity in the curve of electromotive force, that a compound exists in the series of copper-tin, copper-zinc, and gold-tin alloys, and I have also shown that in the alloy between tin, lead, zinc, and cadmium a very small quantity of the more positive metal in the alloy produces its full E.M.F., thus apparently indicating that the metals are merely mixed together. I am at present engaged in applying the method to all the alloys described in Matthiessen's paper on "Electric Conductivity" (*Phil. Mag.*, cl., 1860, 161), but in the meantime there are certain isolated points which seem worthy of being put on record. In the first place I have found indications of a third group of alloys which neither give at once the E.M.F. of the more positive metal, nor show any abrupt discontinuity in the curve of E.M.F. on passing over a particular alloy. In these alloys the E.M.F. rises rapidly, and a continuous curve to the value of the more positive metal as we pass through alloys containing more and more of the more positive metal in the mixture. This curve so closely resembles the curve obtained on increasing the amount of free iodine present in solution in an iodine cell as to suggest at once that these metals correspond in their behaviour to each other to the solution of one substance in another rather than the formation of a compound having a definite formula. If, for instance, we take antimony and lead, and measure the E.M.F. of antimony against lead, we shall find that lead is the more positive metal, and testing antimony against alloys of antimony containing increasing quantities of lead, the E.M.F. gradually rises in a continuous curve.

The readings were taken with both the alloy and the antimony in a cell of sodium chloride.

Alloy.	E.M.F.
Antimony containing—	
4·76 per cent lead—antimony	0·123 volt.
9·05 „ „ „	0·169 „
13·4 „ „ „	0·182 „
16·8 „ „ „	0·215 „
Antimony—lead	0·246 „

These readings were taken with a fresh set of alloys (at a future date to the last), also in a single cell of sodium chloride.

Alloy.	E.M.F.
Antimony containing—	
4·74 per cent lead—antimony	0·057 volt.
9·209 „ „ „	0·112 „
13·03 „ „ „	0·134 „
17·03 „ „ „	0·155 „
Antimony against lead	0·207 „

Another set of readings taken with the same set of alloys as in Table II., only with the antimony in an inner cell containing antimony chloride, and the alloy in an outer cell containing sodium chloride, gave the following results:—

Alloy.	E.M.F.
Antimony—antimony	0·285 volt.
Antimony containing—	
4·74 per cent lead—antimony	0·358 „
9·209 „ „ „	0·415 „
13·03 „ „ „	0·434 „
17·03 „ „ „	0·475 „
Antimony—lead	0·494 „

Another set of readings taken with the same alloys under the same conditions as before, except that the alloys were in an outer cell of potassium nitrate, gave the following results:—

Alloy.	E.M.F.
Antimony—antimony	0·259 volt.
Antimony containing—	
4·74 per cent lead—antimony	0·342 „
9·209 „ „ „	0·386 „
13·03 „ „ „	0·413 „
17·03 „ „ „	0·415 „
Lead—antimony	0·456 „

The same set of alloys read again with the alloy in an outer cell of magnesium sulphate.

Alloy.	E.M.F.
Antimony—antimony	0·254 volt.
Antimony containing—	
4·74 per cent lead—antimony	0·2903 „
9·209 „ „ „	0·342 „
13·031 „ „ „	0·386 „
17·03 „ „ „	0·435 „
Antimony—lead	0·451 „

It will be noticed that in each of these tables the E.M.F. rises rapidly in a continuous curve. Other examples of alloys which behave in this way will be given in a paper on Matthiessen's work. It may be of interest to note here in passing that alloys of this type seem to be apt to yield very inconsistent readings. This can be very easily understood. When the metals are merely mixed

together, some portion of the free metal may be expected to be present on the surface of the alloy, and produce its effect on the electrometer; or when an actual chemical combination has taken place, we may expect to find that all the metal has combined which can combine, and consequently a want of equal mixture between the compound, and the metal which is present in excess will not affect the electrometer, but where the bond is so loose, as in cases of solution where, at the same time, a certain loss of energy has taken place during that solution, we might expect to find different parts of the same alloy, or the same alloy made up on different occasions, giving inconsistent results. Another interesting subject is the result of amalgamating alloys with mercury. In the case of the copper-tin and copper-zinc alloys, I found that amalgamation with mercury did not appreciably affect the electrometer readings, the discontinuity on passing the compound appearing as before. This seemed to indicate that the compound formed between the two metals was sufficiently stable to dissolve in mercury without being decomposed, but in the case of the gold-tin alloys the case is different. In the accompanying table I give the readings in the first column of the E.M.F. of gold-tin alloys against gold in a solution of common salt; while the absolute readings are different, the form of the curve is practically the same as that published by me in the *Philosophical Magazine*, from readings obtained in a stannous chloride gold chloride cell. The second column contains the readings after amalgamation with mercury. It will be noted that these form a gradually ascending line, and that all trace of the compound has disappeared. I can only suppose that the mercury present decomposes the compound. This behaviour of gold, tin, and mercury so closely resembles the replacement of one element by another in a compound, that it led me to look further for indications of such changes, and for this purpose I selected the three metals copper, tin, zinc, as explained in my former papers; the indications of the electrometer readings seemed to show the existence of a compound between copper and tin having the formula of Cu_3Sn, and a compound between copper and zinc having a formula of $CuZn_2$. First of all, therefore, an alloy was made containing 35 per cent of tin, which was just a little less than that necessary to form a compound. The E.M.F. between copper and tin, copper and zinc, copper and the copper-tin compound was then taken in a solution of common salt. Having done this, the copper-tin compound was fused with a weight of zinc equal to the copper contained, the assumption being that if the zinc did not combine with the copper, the E.M.F. of the three metals fused together would be the same as that of the zinc against copper, which is much the highest E.M.F. of the three; while if, on the other hand, the zinc combined with the copper and threw out the tin, the fused metals might be expected to give the E.M.F. of tin. The following table shows the results of the measurements:—

Alloy.	E.M.F.
Copper against tin	0·272 volt.
„ „ zinc	0·84 „
„ containing 50 per cent Zn—	
copper	0·097 „
(Alloy of) zinc 50 per cent, tin 35 per cent, copper—copper	0·25 „

It will be noticed that the E.M.F. of the three metals fused together is almost exactly the same as that obtained from tin, showing apparently that zinc replaces tin in its compound with copper. There is another subject to which I have directed some attention with only negative results. It is a remarkable fact, of which sufficient notice does not seem to have been taken, that so few metals seem to combine with each other; even those which lie close together in the periodic table, enter into combination, while metals which lie far apart on the table refuse to combine. One possible explanation of this which occurred to me was that the temperature at which the metals fused, the compounds formed dissociated, and if the temperature could be lowered sufficiently while keeping them fluid they might be persuaded to combine. I therefore attempted to get zinc and lead to combine by lowering the melting-point by the introduction of bismuth and bismuth mercury, and allowing the alloys to cool slowly in a bath of oil; in every case, however, the E.M.F. of zinc was obtained from the mixture of metals, so that the explanation does not seem to lie in this direction. It is a subject well worthy of enquiry and experiment, as we are unaware at present how many elements there are which do not combine with one another, and we have no indication of the properties of the elements by which this absence of combination is constituted.

NOTICES OF BOOKS.

The Gas Engineers' Laboratory Handbook. By John Hornby, F.I.C. London: E. and F. N. Spon. New York: Spon and Chamberlain. 1894.

The object of this book, as its title implies, is to describe the various analytical processes which are required in gas works. The operations incidental to the carrying out of chemical analysis are described in detail, and, further, the methods of analysing certain substances which are obtainable in a pure state, and are, moreover, typical of those analyses required in gas works, are described minutely.

The preliminary operations, such as the use of the balance, the various steps of sampling, dissolving, precipitating, filtering, &c., which are given *in extenso* in Part I. are, we think, superfluous; there are many books for beginners wherein all this may be learnt, and any young man employed in the laboratory of a gas works would naturally be supposed to have all these details at his fingers' ends.

Part II. describes various simple gravimetric estimations, such as the estimation of SO_4, barium, iron, &c.; and in Part III. we come to volumetric analysis. This is an important branch of laboratory routine; many estimations are simplified and accelerated by its means, while the application of new indicators is constantly adding to the list of bodies which can be determined in this manner.

Part IV. is devoted to special analyses required in gas works, and it is here that the real value of the book commences. Every operation, from the proximate analysis of coal, the estimation of impurities, both in crude and purified gas, to the analysis and estimation of by-products, and substances, such as limestone, oxide of iron, &c., used in the various purifying operations, is here given; and in Part V., which follows, we find detailed descriptions of the technical analysis of the gas itself. These two chapters will be, no doubt, of great service to gas engineers, as everyone is liable to get out of practice, and reference to these pages will soon call back to memory many little details of manipulation which may have been forgotten.

The appendix gives the Gas Referee's instructions as to the time and nature of the various daily tests to be made, and concludes with the necessary tables which assist so greatly in calculating results.

A small list of errata facing page 1 must not be overlooked; one or two of these corrections being of some importance.

Bulletin of the Sugar Experiment Station, Audubon Park, New Orleans, La. By W. C. Stubbs, Ph.D., Director. Issued by the Bureau of Agriculture. Nos. 24 and 26. 1894.

The physiological and physical experiments herein described and tabulated were carried out during the past

two years at the Sugar Experiment Station in New Orleans. For a long time back the Commissioners of Agriculture in the United States have been carrying on similar experiments in many parts of the country, and they hope the results will be properly studied and applied by the farmers and planters they are intended to benefit.

The results of one year only are, of necessity, frequently misleading, the variations of climatic and other conditions being so great. Many of the experiments have been repeated as exactly as possible for a period of over eight years, and several valuable suggestions have been secured, though nothing in many instances of a positive nature has been obtained.

The experiments are divided under the following heads, viz.:—

1. Physical, *i.e.*, meteorological, preparation and cultivation of the soil, irrigation, and drainage.
2. Physiological.
3. Foreign varieties of cane.
4. Comparison of home varieties, the ribbon and purple.
5. Manurial requirements of cane.
6. Economic, *i.e.*, testing the best methods of preserving cane to prolong the grinding season.

It will be seen that these headings cover an extremely wide field, and there is no doubt that the farmers should, in these times of acute competition, take advantage of every suggestion which will reduce the cost of production and increase the yield.

The United States appears to be more go-ahead than the Old Country in these matters. If more attention were paid to improving agriculture by those in authority in these islands, we might possibly ere long hear less of that disheartening theme "depression of trade."

Agricultural Journal. Published by the Department of Agriculture of the Cape Colony. Vol. VII., No. 9.

THIS journal continues its career of usefulness and is replete with valuable matter, much of which, however, is more biological than chemical. Several fungicides are recommended for application to fruit trees, potato-fields, &c. Of these, the strong Bordeaux mixture (6 lbs. copper sulphate, 4 lbs. lime, to 22 gallons water) has given the best results. Ammoniacal copper carbonate has proved a failure.

The editorial remarks in glorification of beet-sugar omit one of the causes of its success. Protective duties and export bounties in its favour have played no unimportant part on its behalf. We believe that if the same "scientific cultivation and chemistry" had been applied to the cane, beet-sugar, despite protectionism, would have been fairly beaten out of the field.

In the paper on "Green Manuring," the merits of G. Ville ought, we think, not to have been overlooked.

A new remedy for the phylloxera, accidentally discovered, consists in planting sumac bushes (*Rhus coriaria*) among the vines. The climates both of South Africa and of many parts of Australia are, we believe, well adapted for the growth of this shrub, and its leaves are in constant demand among dyers.

In the question of "dogs *v.* poison" for the destruction of noxious beasts, none of the speakers seem to have reflected that dogs are the chief agents for spreading hydatid disease. Hence they should be absolutely debarred all access to public water supplies, aqueducts, filter-beds, &c. In some parts of Australia hydatidous cysts are alarmingly prevalent.

Zeitschrift fur Elektrotechnik und Elektrochemie. Halle: Wilhelm Knapp. No. 2, 1894.

Elektrochemische Zeitschrift. Berlin: Fischer and Heilmann. No. 2, 1894.

WE are glad to welcome these two latest additions to electrical journalism, of which the second numbers have just reached us. They are similar in style and object, and besides various articles on electrical subjects, such as electric railways, arc lamps, &c., several pages are devoted to correspondence, reviews, and recent patents. The letterpress is happily in English characters, rendering its perusal much less trying to the eyes than are so many German papers. We wish our young contemporaries every success.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxviii., No. 24, June 11, 1894.

A correspondent for the Chemical Section was elected *vice* the late Dr. de Marignac. Prof. Cannizzaro was returned by a large majority of votes as against Prof. Mendeleeff, the only other candidate.

Green Pigment in the Phyllia an Orthopterous Group of the Family of the Phasmidæ.—Henri Becquerel and Charles Brongniart.—For a long time chlorophyll has been considered as existing only in plants, and when this substance has been detected in animals it has been almost always recognised as chlorophyll contained in the digestive channels or belonging to parasitical algæ which live with the animals in a state of symbiosis. Still chlorophyll has also been found in a diffused state in certain infusoria, which appear to have formed it from its elements. This fact has not yet been established among insects. In these there are some in which the green colouration is due to a pigment which has nothing in common with chlorophyll. Others, on the contrary, such as certain orthoptera of the family of Phasmidæ, the phillia, resemble green leaves so closely that we are led to ascribe their green colour to chlorophyll. On careful spectroscopic examination it is found that its absorption bands do not differ from those observed through living leaves, and they are consequently due to chlorophyll.

Homologues of Quinine: their Physiological and Therapeutic Action.—E. Grimaux, assisted by MM. Laborde and Bourru.—The author finds that cupreine, the base obtained from *Quina cuprea*, is a substance of a mixed function, an alkaloid phenol. Its methyl compound is identical with quinine. He has obtained the following series:—

$C_{19}H_{21}N_2O,OH$, cupreine.
$C_{19}H_{21}N_2O,OCH_3$, methyl-cupreine (quinine).
$C_{19}H_{21}N_2O,OC_2H_5$, ethyl-cupreine (quinethyline).
$C_{19}H_{21}N_2O,OC_3H_7$, propyl-cupreine (quinopropyline).
$O_{19}H_{21}N_2O,OC_5H_{11}$, amyl-cupreine (quinamyline).

Ethyl-cupreine as an anti-periodic is found much superior to quinine.

Determination of Iodine.—A. Villiers and M. Fayolle.—This paper will be inserted in full.

Acid Aniline Ortho- and Paratoluidine Sulphates.—Edmond Hitzel.—These compounds do not seem to have been previously obtained. They are easily prepared by superposing a solution of the neutral sulphates saturated in heat over a stratum of concentrated sulphuric acid in a large vessel. The whole is then refrigerated at least to 0°. In from twelve to twenty-four hours the upper stratum of the liquid is filled with fine crystals of the acid salt. These sulphates are stable in dry air, but hygroscopic, and if placed in contact with solvents they become opaque and are decomposed; if exposed to a

temperature of 100° they are gradually modified and become coloured. The composition of the aniline salt is $SO_4H_2(C_6H_7N)+\frac{1}{2}H_2O$. The method of preparing acid salts by slow diffusion and simultaneous refrigeration may perhaps be applicable to other cases.

Synthesis of Hexamethylenic Derivatives. — A. Combes.—Not adapted for useful abridgment.

Qualitative Composition of the Officinal Creosotes of Beech-tar and Oak-tar.—A. Béhal and E. Choay.—By officinal creosotes the authors understand the total phenols which distil over between 200° and 220°. Qualitatively the two creosotes are identical in composition. They are very complex mixtures, in which we have identified and isolated the following substances :—Phenol, orthocresylol, paracresylol, orthoethylphenol, metaxylenol (1.3.4), metaxylenol (1.3.5), gayacol, creosol, and ethylgayacol. Besides these substances, creosote contains small quantities of sulphur derivatives, probably thiophenols and a body differing from pittacol, but which on exposure to air and ammonia gives rise to a substance which dissolves in alkalis with an intense blue colour, and which is reddened by acids. These properties to some extent approximate it to orceine, which Liebermann has shown to be a mixture.

Action of Primary Aromatic Bases upon Asymmetric Ketonic Bases.—L. Simon.—These researches have been undertaken with the prospect of discovering in anilic compounds of the form—

$$\begin{matrix} R-C-R' \\ \| \\ N-C_6H_5 \end{matrix},$$

isomeric manifestations analogous to those which have been fully established for the oximes, and of which some instances have recently been observed in the hydrazones. Nothing of the kind has been traced.

Stability of the Aqueous Solutions of Mercuric Chloride.—E. Burcker.—The author concludes from his experiments that common waters, on account of the substances which they contain, cause the immediate decomposition of mercuric chloride. The decomposition continues under the influence of air, light, and of the mineral and organic matters present in the water or introduced by the air. The decomposition ceases or becomes insignificant if the solution is withdrawn from the action of air and light. The solutions of mercuric chloride prepared with pure distilled water undergo merely insignificant decompositions even when they remain exposed to air and light.

The Preparation of Ethylene Perchloride and its Behaviour with Ozonised Oxygen.—A. Besson.—The author has obtained the ethylene perchloride by using as the primary material CCl_4. The reaction of aluminium filings with CCl_4 is promoted by the presence of iodine; if the temperature is slightly raised by means of the water-bath, the reaction continues. The action of white phosphorus is explosive about 200°. Ozonised oxygen reacts badly upon C_2Cl_4 at 0°, but at 30° the ozone is fixed and there are liberated small quantities of oxychloride, $COCl_2$.

A Ptomaine obtained from the Urine of Cancer Patients.—Dr. A. B. Griffiths.—The method used for the extraction of this ptomaine has been described (*C. R.*, cxiii., p. 656). It is a white substance crystallising in microscopic needles, soluble in water, and having an alkaline reaction. It forms a chloroplatinate, a chloraurate, and a hydrochlorate. With phosphotungstic acid it gives a yellow precipitate, with phosphomolybdic a brown, and with silver nitrate a red. Mercuric chloride produces with it a grey precipitate, and Nessler's reagent a brownish precipitate. Its composition is $C_8H_5NO_5$. It is very poisonous, producing fever and death in three hours. Cancerine, as the author names it, is not present in normal urine, but is formed in the system in the course of *Cancer Uteri*.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., No. 7.

New Apparatus for Fractionated Distillation.—Eugene Varenne.—This paper requires the two accompanying figures.

Experiments on Splitting up Non-saturated Substances.—A. Le Bel.—The author has employed the agency of moulds and other microphytes. The results were falsified by the fixation of water observed. On the other hand, it may be concluded from this research that the first derivatives of ethylene have really the plane form which has been ascribed to them.

Preparation of Nitroso-propionate (Nitroso-propanoate) of Ethyl.—G. Lepercq.—The author's procedure increases the yield of nitrous ether five-fold. It has the advantage of being applicable to the fatty acids higher than the propionic acid, to the ethyl- and methyl-bromobutyrates, to methyl-bromo-isobutyrate, to ethyl-bromovalerate when it gives crystalline products analogous in aspect to that of ethyl-nitroso-propionate.

Reaction of Methyl-bromo-propionate with Sodium Nitrite.—G. Lepercq.—The first product of this reaction is nitropropionic ether. A portion of this is converted into dinitroso-dilactic ether by elimination of water between two molecules. Another portion passes into the state of methyl-nitroso-propionate. The chief part is decomposed in contact with the excess of alkaline nitrite, yielding carbonic acid and nitrolate, the formation of which explains the colouration of the product, yellow at first and afterwards red. The nitrolate is decomposed partially into acetate and a mixture of nitrogen and nitric oxide.

Preparation of Valerianic Aldehyd.—L. Bouveault and L. Rousset.—The authors have modified the method published in the works of Würtz and Beilstein so as to obtain 60 per cent of the alcohol employed as pure aldehyd.

Chloralose.—M. Hanriot and Ch. Richet.—A reply to revision of their memoir by Petit and Polanowsky. The authors submit that the work of the chemists named confirms their experiments and their formula, and brings forward an interesting fact, *i.e.*, the decomposition of chloralose into its constituents by the prolonged action of relatively concentrated acids.

Tetra-substituted Tartaric Ethers.—P. Freundler.—This voluminous memoir does not admit of useful abstraction.

Para-amidoacetophenone and the Secondary Para-amidophenylethylic Alcohol.—L. Rousset.—The alcohol is soluble in cold water, but it dissolves more readily in boiling water, from which it is deposited in pure white crystals. It is equally soluble in alcohol, ether, chloroform, benzene, and the acids. It turns yellow on exposure to light.

Dibromogallanilide and its Triacetylic Ether.—P. Cazeneuve.—It forms small white needles of the composition $C_6Br_2\begin{cases} CO.NH.C_6H_8 \\ (OH)_3 \end{cases}$

Determination of Mannite by the Optical Method.—J. A. Müller.—The author has ascertained that the mannite of wine is identical with the mannite of manna. In the wines examined there are not, in addition to mannite, appreciable quantities of other sugars sparingly soluble in alcohol and water in the cold and not precipitable by basic lead acetate.

Correction in the Determination of Standard of a Liquid Holding a Precipitate in Solution. Application to Saccharimetry.—E. Lenoble.—This paper will be noticed by opportunity at some length.

Loss of the Charge of Sulphuric Acid in the Lead Pipes. — A. Lambert. — This paper requires the two accompanying figures.

MEETINGS FOR THE WEEK.

Monday, July 2nd.—Royal Institution, 5. General Monthly Meeting.
Friday, 6th.—Geologists' Association, 8.

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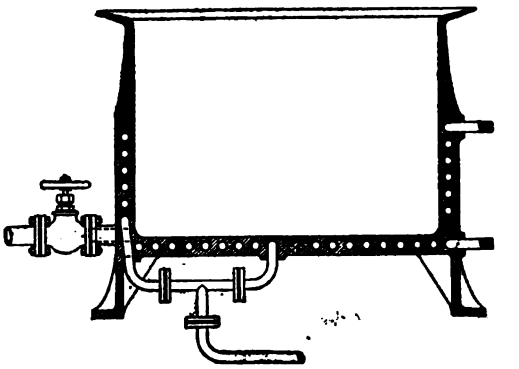

Mr. C. R. ALDER WRIGHT, Lecturer on Chemistry and Examiner in Soap to the City and Guilds of London Institute, in his latest edition of "Animal and Vegetable Oils, Fats, Butters, and Waxes, &c." (Charles Griffin and Co., Lim., London, 1894), says:—

P. 316. "An improved vessel for boiling oil, and suitable for many other kindred purposes, has been recently described by T. Frederking (Chemical News, London). A coil of stout piping is arranged in a casting mould, so that the molten metal forming the pan is cast round the coil, much as is done in the case of the water-tuyeres of a blast furnace. Steam at any pressure [or any other heating medium] being passed through the coil, the pan is heated up proportionately without any danger, the pressure bearing solely on the piping and not on the metal pan itself, whilst the well conducting metal walls allow the heat to pass readily. Temperatures up to 350° and 400° C. can be thus obtained."

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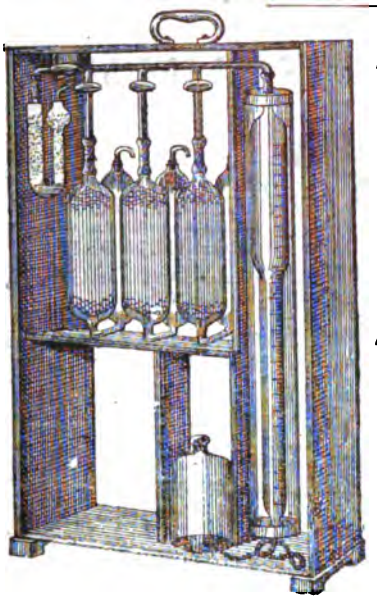

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